

UNIVERSITY OF ILLINOIS
LIBRARY

Class

666

Book

IL6

Volume

1-15

cop. 1

The person charging this material is responsible for its return to the library from which it was withdrawn on or before the **Latest Date** stamped below.

Theft, mutilation, and underlining of books are reasons for disciplinary action and may result in dismissal from the University.

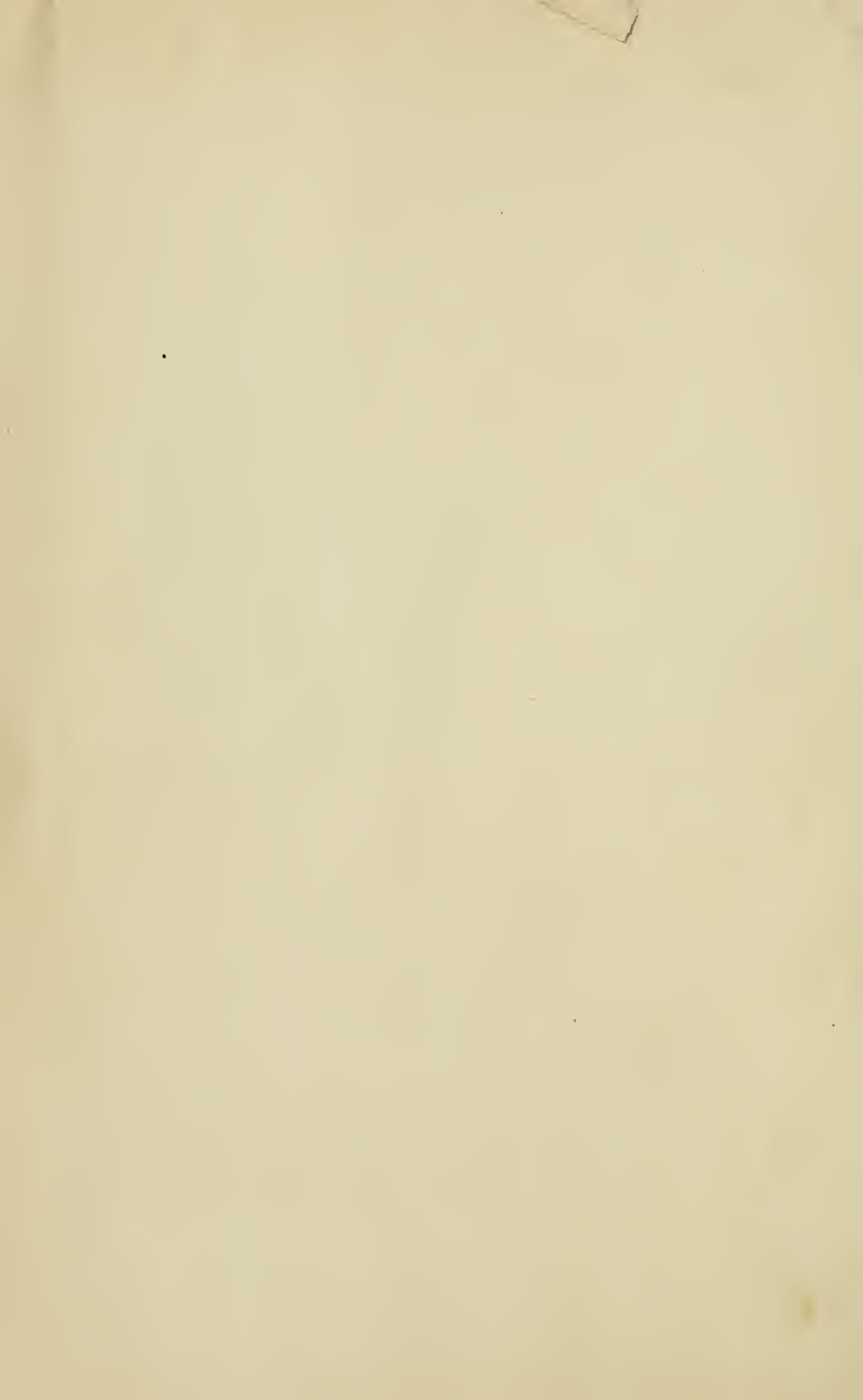
UNIVERSITY OF ILLINOIS LIBRARY AT URBANA-CHAMPAIGN

FEB 9 1976

JAN 16 1976

SEP 18 2001

MAY 32 2001



UNIVERSITY OF ILLINOIS BULLETIN

Vol. 4.

FEBRUARY 15, 1907

No. 12

[Entered at Urbana, Illinois, as second-class matter]

STUDIES FROM THE SCHOOL OF CERAMICS

NUMBER TWO.

STUDIES IN GLAZES.

PART I.

FRITTED GLAZES.

BY

R. C. PURDY AND H. B. FOX.

PUBLISHED FORTNIGHTLY BY THE UNIVERSITY



FRITTED GLAZES; A STUDY OF VARIATIONS OF THE OXYGEN RATIO AND THE SILICA-BORACIC ACID MOLECULAR RATIO.

BY

ROSS C. PURDY AND HARRY B. FOX, Champaign, Ills.

Two systematic studies of raw lead glazes, published in the Transactions of the American Ceramic Society, have done much to indicate the limits of variation in their composition and heat treatment.

Accounts of similar studies of fritted glazes could not be found by the writers, after a search in the literature of ceramics. This want of definite information is certainly not because fritted glazes are unimportant or little used, for, on the contrary, they form the basis of decoration for the most costly wares, and are to the white-ware manufacturer the glaze *par excellence* in the making of non-crazing china.

This dearth of information regarding fritted glazes is no doubt due largely to their complexity in composition and the consequent difficulties in making the necessary calculations. When there are but two variables as in the case of raw lead glazes, only the simplest calculations are required to formulate series in which one or both numbers vary in some predetermined ratio, but when three variable factors are to be considered, as in the case of fritted glazes, the planning of a like series presents serious difficulties.

Mr. Ashley¹, in his able discussion of the two papers on the composition of biscuit bodies that appeared in Volume VII of the Transactions, demonstrated clearly the incompleteness that is apt to follow an attempt to determine the limits of variation of three factors when taken in pairs

¹Trans. Am. Cer. Soc., Vol. VII, p. 90.

in six or more wholly independent series. As a further illustration, several series of fritted glaze studies were formulated, in each of which either the Al_2O_3 , SiO_2 or B_2O_3 was varied in an arithmetical ratio. Several good glazes were developed in each series, and consequently it was thought a very wide range in the composition of fritted glazes at certain temperatures had been determined. Such, however, did not prove to be the case, for, when the glazes had been compared as to their oxygen ratio, $\text{SiO}_2\text{—B}_2\text{O}_3$ ratio, and Al_2O_3 content, it was found that but a very narrow range in composition had been used. As a result, the large amount of experimenting had practically been for naught.

Confident that the difficulties in the case of fritted glazes could be overcome, the senior writer gave considerable thought to methods by which the range in the variations of the three factors, Al_2O_3 , SiO_2 , and B_2O_3 could be determined. The one given in the following report seemed to be the most feasible for the purpose. Many improvements in the details of the original plan were made by the junior writer, and it is felt that the method as here presented is simple in its detail, and permits a very broad study of the limits of variation in fritted glaze composition.

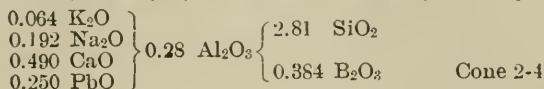
There are important details of the fritted glaze problem which cannot be determined by any consideration of the oxygen ratio, the molecular ratio, nor in some cases, even the ultimate chemical formulae of the glazes. As an illustration, oxygen ratio does not seem to be a factor in determining the kind and quantity of the several ingredients that should be incorporated into the fritt, and what should be added 'raw', in order to obtain a given fusibility, coefficient of expansion and contraction, fluidity, solvent effect on body, production of color tints, etc., etc., consequently such questions are not considered in the experiments here reported, although as stated before, their importance is recognized.

Owing to the scarcity of reliable scientific data on the fritted glazes actually used in the different ceramic indus-

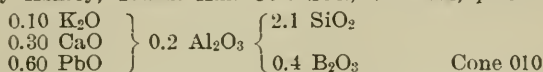
tries, but very little idea of the limits of variation in the composition and heat treatment of such glazes could be obtained.

The following are a few of the formulae studied:

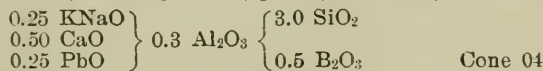
White Ware Glaze, E. Mayer, Trans. Am. Cer. Soc., Vol. I, p. 57.



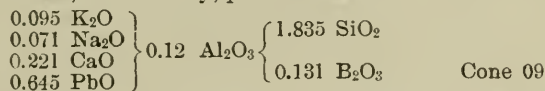
Earthen-ware Glaze, Dr. H. Hecht, Thonindustrie-Zeitung, 1897, quoted by Ashley, Trans. Am. Cer. Soc., Vol. VII, p. 92.



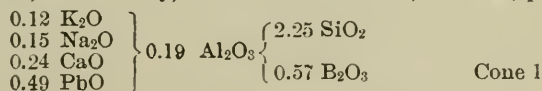
White Ware Glaze, K. Langenbeck, p. 122, Chemistry of Pottery.



Wall Tile Glaze, R. C. Purdy, private notes.



Wall Tile Glaze, R. C. Purdy, Trans. Am. Cer. Soc., Vol. VII, p. 81.



GENERAL PLAN OF INVESTIGATION.

A study of these successful commercial fritted glazes revealed the fact that there were four factors to be considered in the make-up of the chemical formulæ.

1st. The character of R. O. i. e. the kind and equivalent amounts of each present.

2nd. The oxygen ratio, i. e. the ratio of the total oxygen in the acids to the total oxygen in the bases.

3rd. The molecular ratio of the silica to boracic acid.

4th. The equivalent content of alumina.

It is quite obvious that since there are oxides of seven or eight different basic elements used for different purposes in fritted glazes, there are a great many possible RO combinations that could be and should be tried if the study of

the entire field of fritted glazes is to be attempted. Since for each RO there is a large number of possible variations in the other factors, it is evident that it would be impractical to include all possible combinations in one investigation. It was decided, therefore, to limit this study to one arbitrarily chosen RO.

The RO. The following was taken because it represents the average character of the RO used in white-ware and wall-tile glazes.

0.126	Na ₂ O
0.124	K ₂ O
0.500	CaO
0.250	PbO

The Oxygen Ratio. In order to not only cover the range of variation in the oxygen ratio of the commercial fritted glazes studied in the preliminary survey of the subject, but also to determine if possible the practical limits of such variation, it was thought best to go beyond what was taken to be the extreme minimum and maximum. Since the most workable oxygen ratio in a raw lead glaze has been found to be 1:2, and since one of the fundamental objects in the use of fritted glazes is to secure increased acidity and consequent reduction of the coefficient of expansion and contraction, this ratio (1:2) was adopted as the minimum. At the time the study here reported was made, it was thought that the oxygen ratio of 1:4 was the maximum in use, and therefore a ratio that would represent a step beyond this limit was chosen as the maximum.

During the progress of the investigation it was found that the maximum limit possible under all conditions had not been chosen, for, not only, were there good glazes developed with this oxygen ratio, but it has since been found that Seger had used leadless barium fritted glazes that ranged as high as 1:6 with reported success.

The following are the oxygen ratios adopted:

Oxygen in Total Bases	Oxygen in Total Acids
1	2.00
1	2.50
1	3.00
1	3.50
1	3.75
1	4.00
1	4.50

The Silica-Boracic Acid Molecular Ratio. It was inferred from a study of commercial fritted glazes that the silica-boracic acid molecular ratios varied from 1:0 to 1:0.20, and therefore 1:0.25 was chosen as the maximum. Here also it has since been learned that the possible maximum ratio was not adopted, for Edwards and Wilson¹ report the successful use of a much higher ratio.

The silica-boracic acid ratios adopted in this study were:

$$\frac{1}{0.25}; \frac{1}{0.20}; \frac{1}{0.17}; \frac{1}{0.13}; \frac{1}{0.09}; \frac{1}{0.05}; \frac{1}{0.01} \text{ and } \frac{1}{0}.$$

The Range in Alumina Content. It is quite obvious to those who have made a study of glazes in general, that the permissible maximum equivalent of Al_2O_3 is dependent upon the temperature at which the glaze is designed to mature, and since cone 10 had been arbitrarily chosen as the maximum temperature at which to burn the glazes of this study, it was decided that 0.45 equivalent would be a larger equivalent than would be used commercially in the vast majority of instances. It is common experience that a small equivalent of Al_2O_3 is quite necessary to the development of an insoluble or stable glaze, and that as a rule white ware glazes contain from 0.25 to 0.40 equivalents. It

¹Trans. Eng. C. S. 1904-5, p. 24.

was thought, therefore, that 0.1 equivalents could, with justice to the study, be considered as the minimum amount feasible.

The equivalent molecular variations of Al_2O_3 chosen were 0.1; 0.15; 0.20; 0.25; 0.30; 0.35; 0.40 and 0.45.

Shown in tabular form these three variable factors can be represented as follows:

Division into Groups by Oxygen Ratio		Division of Groups into Series by the Molecular Ratio of $\text{SiO}_2 : \text{B}_2\text{O}_3$		Division of Series into Members Differentiated by their Al_2O_3 content	
Group No.	O. R.	Series No.	Ratio	Member Designation	Al_2O_3 Equiv.
I	2.00	1	1 : 0.25	a	0.10
II	2.50	2	1 : 0.20	b	0.15
III	3.00	3	1 : 0.17	c	0.20
IV	3.50	4	1 : 0.13	d	0.25
V	3.75	5	1 : 0.09	e	0.30
VI	4.00	6	1 : 0.05	f	0.35
VII	4.50	7	1 : 0.01	g	0.40
		8	1 : 0.00	h	0.45

CALCULATION OF THE GLAZES.

The calculation of the proportions in which the various extremes in these series are to be blended to produce any given glaze of the 448 provided for in the above scheme is somewhat perplexing, and as before stated, was made the subject of a good deal of thought. The following method of calculation was finally found to be the most satisfactory. Considerable more space is given therefore to the detailed explanation of the method than would perhaps be justifiable in ordinary cases.

First Method: Formula of Glazes. The oxygen ratio of a fritted glaze can be expressed by the formula

$$(A) \quad \text{O.R.} = \frac{2y+3z}{3x+1}$$

in which O. R. stands for oxygen ratio; y represents the molecular equivalent of SiO_2 present; z the molecular equivalent of boracic acid; x the molecular equivalent of alumina; and the numeral 1, the oxygen in the RO when the total equivalent of RO is reduced to unity. In the

statement of conditions for any one glaze, the oxygen ratio and alumina equivalent are given, i. e. known. Each formula thus contains only y and z as unknowns. Since the ratio of y to z is also given in the silica-boracic acid ratio, we have the equation

$$(B) \quad y : z :: 1 : b \text{ or } z = by.$$

With these two simultaneous equations y and z are readily determined.

Since the Al_2O_3 equivalent varies regularly in each series, it is quite obvious that the SiO_2 and B_2O_3 content of the several glazes in each series differs by a constant factor that can be obtained by subtracting the SiO_2 and B_2O_3 in the first member (a) from the SiO_2 , and B_2O_3 equivalent in the second (b), so that only the first two members of the series need be calculated by equations (A) and (B).

Second Method. It was developed in the actual carrying out of the calculations by the first method that only the first two terms of the series in the end groups need be calculated by the above equations. After obtaining the SiO_2 and B_2O_3 for the members of each series in Groups I and VII as given in the first method, the corresponding serial members of the intermediate groups, it was found, could be obtained by a blending calculation on the basis of the difference in the oxygen ratio and the rule of extreme and mean differences. The blending factors for the groups are

		Parts of Group I	Parts of Group VII
Group	I.....	1.0	0.0
"	II.....	0.8	0.2
"	III.....	0.6	0.4
"	IV.....	0.4	0.6
"	V.....	0.2	0.7
"	VI.....	0.2	0.8
"	VII.....	0.0	1.0

Equiv. SiO_2 for S I, G I "a" (.9454) times 0.8 = 0.75632

" " " S I, G VII "a" (2 1' 3) times 0.2 = 0.42547

" " " S I, G II "a" then $0.75632 + 0.42546$ or 1.1818

By this method the SiO_2 and B_2O_3 content of the glazes in all the groups can be very readily obtained by the use of simple factors as above shown.

Blending of the Glazes.

There are many ways in which the glazes indicated in the above table could be blended, but it was decided that this could be done most readily and with the greatest accuracy when the number of "original" or weighed glaze batches was the smallest, so that the fritts might be melted in large quantities at one time, and thus errors in weighing fractional quantities made as small as possible. Each individual glaze can then be made by weighing portions of these few made-up glazes as explained later.

The minimum number of "weighed" glazes that could be used in this blending scheme was found to be eight, as follows:

1.	Group I.	Series 1 member a
2.	Group I.	" 1 " h
3.	Group I.	" 8 " a
4.	Group I.	" 8 " h
5.	Group VII.	" 1 " a
6.	Group VII.	" 1 " h
7.	Group VII.	" 8 " a
8.	Group VII.	" 8 " h

Of these eight glazes the first four are from Group I and the last four are from Group VII. In the first group, therefore, the maximum amount of each of the first set of four glazes will be used and in Group VII the maximum amount of each of the last set of four glazes. The amounts of the glazes in each set that are used in the intervening groups are in the same proportion as the oxygen ratio of those several groups. By again noting the extreme and consecutive variations in oxygen ratios in the tabulated statement of the groups and series, it will be seen that these proportional amounts for each group as noted above are as follows:

Group I	1.0	0.0
Group II	0.8	0.2
Group III	0.6	0.4
Group IV	0.4	0.6
Group V	0.3	0.7
Group VI	0.2	0.8
Group VII	0.0	1.0
Total,	3.3	3.7

That is, in the first group, 10-33 of the total amount of the first four weighed glazes will be used; in the second group 8-33 of the first four and 2-37 of the second four, etc.

Having thus calculated the distribution of the eight weighed glazes in the several groups, the next step is obviously the determination of the proportional amount of each of the "weighed" glazes in each series.

Since the "weighed" glazes represent series 1 and 8 of each group, by making blending calculations on the basis of the silica content, the intermediate series of each group are made up of proportional parts of the extreme series as follows:

Series	Weighed Glazes of 1st Series	Weighed Glazes of 8th Series
1	1.0000	0.0000
2	0.8461	0.1539
3	0.7451	0.2549
4	0.5984	0.4016
5	0.4363	0.5637
6	0.2558	0.7442
7	0.0542	0.9458
8	0.0000	1.0000
Total	3.9359	4.0641

To illustrate how this proportional distribution of the weighed glazes is made in the separate groups take Group II, Series 4. It was determined that for Group II there should be used 8-33rds of the total amount of the weighed glazes belonging to Group I and 2-37ths of the

weighed glazes belonging to Group VII. In Series 4, of Group II, therefore, there would be used :

$$\left(\frac{0.5984}{3.9359} \times \frac{8}{33} \right) \text{ of weighed glaze 1 and 2.}$$

$$\left(\frac{0.5984}{3.9359} \times \frac{2}{37} \right) \text{ of weighed glaze 5 and 6.}$$

$$\left(\frac{0.4016}{4.0641} \times \frac{8}{33} \right) \text{ of weighed glaze 3 and 4.}$$

$$\left(\frac{0.4016}{4.0641} \times \frac{2}{37} \right) \text{ of weighed glaze 7 and 8.}$$

Similar calculations were made for each series in each of the groups.

The sum or mixture of the proportional parts of the total amount of "weighed" glazes 1, 3, 5, and 7, as shown above, would constitute the first member or "a" of Series 4, Group II and the mixture of the proportional parts of the total amount of "weighed" glazes 2, 4, 6, and 8, as above shown, would constitute the last member or "h" of Series 4, Group II.

Having thus the proportional part of the total amount of the "weighed" glazes in the first and last members of each series in each of the groups, the further distribution of the "weighed" glazes in the intermediate members of each series must be made on the blending proportions as obtained on the basis of the difference between the alumina content of each member. These proportional factors are found to be as follows :

Members of Series	Proportion of "a" in each Member	Proportion of "b" in each Member
a	1.0000	0.0000
b	0.8571	0.1429
c	0.7142	0.2858
d	0.5714	0.4286
e	0.4286	0.5714
d	0.2858	0.7142
f	0.1429	0.8571
g	0.0000	1.0000
Total	4.0000	4.0000

Series 4 Group II then may be made up by blending the eight "weighed" glazes in the proportional amount of the total of each of the "weighed" glazes as in the table on page 106-107.

To demonstrate that the factors there developed give true results, the chemical formula of glaze d, Series 4, Group II, is calculated as follows:

	RO	Al ₂ O ₃	SiO ₂	B ₂ O ₃
0.00526 Eqv. glaze No. 1 contains	0.0052	0.0005	0.0049	0.0012
0.00394 " " No. 2 "	0.0039	0.0018	0.0067	0.0016
0.00341 " " No. 3 "	0.0034	0.0003	0.0044
0.00256 " " No. 4 "	0.0025	0.0012	0.0060
0.00117 " " No. 5 "	0.0011	0.0001	0.0025	0.0006
0.00088 " " No. 6 "	0.0008	0.0003	0.0034	0.0008
0.00076 " " No. 7 "	0.0007	0.0001	0.0022
0.00057 " " No. 8 "	0.0005	0.0002	0.0030
Total	0.0181	0.0045	0.0331	0.0042

Multiplying these totals through by an amount which will bring the RO to unity, or 55.24, we have the following result:

$$0.9998 \text{ RO, } 0.2485 \text{ Al}_2\text{O}_3 \left\{ \begin{array}{l} 1.8284 \text{ SiO}_2 \\ 0.2820 \text{ B}_2\text{O}_3 \end{array} \right.$$

of which the oxygen ratio is 1:2.49+

Since the sum of the elements brought in by the respective amounts of the various weighed glazes employed makes a glaze whose formula satisfies all the conditions for glaze 'd', Series 4, Group II, the above method of calculation must be correct in principle.

In the same manner, the equivalent amounts of the eight "weighed" glazes required for a mixture or blend, having the chemical composition of each of the 448 glazes required for the whole investigation can be calculated and tabulated.

These equivalents or factors are parts by molecules but not by weight. In the calculation of the required parts by weight of the eight "weighed" glazes, the total amount of each glaze required, and the difference in the combining

Calculation for Compounding

		Proportion of Weighed Glaze Number 1	Proportion of Weighed Glaze Number 2	Proportion of Weighed Glaze Number 3
a	$\frac{0.5984}{3.9359} \times \frac{8}{33}$	0 0368		0.0239
	$\frac{0.4016}{4.0641} \times \frac{8}{33}$			
	$\frac{0.5984}{3.9359} \times \frac{2}{37}$			
	$\frac{0.4016}{4.0641} \times \frac{2}{37}$			
b	"a" $\times \frac{0.8571}{4.000}$	0 0079		0.00512
	"h" $\times \frac{0.1429}{4.000}$		0.001375	
c	"a" $\times \frac{0.7142}{4.0000}$	0.00657		0.004267
	"h" $\times \frac{0.2858}{4.000}$		0.00263	
d	"a" $\times \frac{0.5714}{4.000}$	0.00526		0.003414
	"h" $\times \frac{0.4286}{4.000}$		0.00394	
e	"a" $\times \frac{0.4286}{4.000}$	0.00394		0.00256
	"h" $\times \frac{0.5714}{4.000}$		0.00526	
f	"a" $\times \frac{0.2858}{4.000}$	0.00263		0.00181
	"h" $\times \frac{0.7142}{4.000}$		0.00657	
g	"a" $\times \frac{0.1429}{4.000}$	0.001315		0.000854
	"h" $\times \frac{0.8571}{4.000}$		0.007885	
h	$\frac{0.5984}{3.9359} \times \frac{8}{33}$		0.0368	
	$\frac{0.4016}{4.0641} \times \frac{2}{37}$			
	$\frac{0.4016}{4.0641} \times \frac{8}{33}$			
	$\frac{0.5984}{3.9359} \times \frac{2}{37}$			

Series 4, Group II.

Proportion of Weighed Glaze Number 4	Proportion of Weighed Glaze Number 5	Proportion of Weighed Glaze Number 6	Proportion of Weighed Glaze Number 7	Proportion of Weighed Glaze Number 8
	0.00822			
			0.00535	
	0.00176		0.001146	
0.000854		0.000294		0.000191
	0.00147		0.00096	
0.00181		0.000587		0.000382
	0.001174		0.00076	
0.00256		0.00088		0.000573
	0.00088		0.000573	
0.003414		0.001174		0.00076
	0.000587		0.000382	
0.004267		0.00147		0.00096
	0.000294		0.000191	
0.00512		0.00176		0.001146
				0.00535
0.0239				
		0.00822		

or batch weights of each of the "weighed" glazes must be considered. This latter consideration has not until lately been noted in the blending of series of glazes or bodies and, so far as the writers can learn, it was first suggested and made use of by the senior writer, in class exercises in ceramics at the Ohio State University in 1903, and was first mentioned in published papers by E. Ogden, who was a student at Ohio at that time.¹ Mr. Ogden has amply set forth the necessity of noting the difference in the batch weights of the extremes, so that further discussion of this point at this time is superfluous. The importance of taking cognizance of the differences in combining weights of the several glazes to be blended is illustrated in the following:

Calculation of required total amount of "weighed" glazes for entire experiment. By trial it was found that about 60 grams of fritted glaze was necessary to make a coating one-sixteenth to one-eighth inch thick on five 3 inch by 1 inch by $1\frac{1}{2}$ inch wall tiles. It is obvious that the maximum quantity of any one of the "weighed" glazes in a given blend would be required in the case where the "weighed" glaze is used alone, or unblended with any of the others. Considering this as a safe criterion by which the total amount of each the "weighed" glazes required in the entire series of blends can be estimated, it is quite obvious that since, in the case of "weighed" glaze No. 1, for illustration, as shown in the development of the blending factors, 10.33 of the total amount is required for the first

1

group; and $\frac{1}{3.9359}$ of the quantity required for the first

group is used in the first series; and $\frac{1}{4}$ of that used in the first series is required in the first member or 'a', it follows

that $\frac{10}{33} \times \frac{1}{3.9359} \times \frac{1}{4}$ or $\frac{10}{519.54}$ of the total amount of

¹Trans. A. C. S., Vol. VII, p. 378.

"weighed" glaze No. 1 used in the entire system of blends
10

must be equal to 60 grams. Therefore $60 \div \frac{10}{519.54}$ or

3117.24 grams is the total amount of "weighed" glaze No. 1 required.

Having calculated the batch weight of the eight "weighed" glazes, as shown later, it was found that the combining weight of "weighed" glaze No. 1 was 213.78.

Since 3117.24 was so nearly 15 times the combining weight of "weighed" glaze No. 1, 15 was adopted as a factor by which the combining weights of each of the eight "weighed" glazes should be multiplied to ascertain the total amount of each required for blending the entire number of glazes in this experiment, as shown in the following table:

Weighed Glazes	Combining Weight	Factor	Amount Required
1	213.78	15	3207
2	293.78	15	4452
3	206.52	15	3097
4	305.34	15	4580
5	293.00	15	4395
6	462.32	15	6935
7	303.97	15	4560
8	481.47	15	7222

Means of Minimizing the Number of Weighings in Above Blending Scheme. By simple calculations it was found that if the above scheme of blending was carried out in detail as given, 2976 separate weighings would be required. By first weighing up the "weighed" glazes proportionally into groups, then thoroughly mixing the blended glazes by passing them through a 60 mesh sieve six or seven times; taking these blended glazes, now 46 in number, and blending them proportionally into series, and then finally into the separate members, in other words, by making the blends in three stages, there would be required only 656 or less than $\frac{1}{4}$ of the number of weighings that would be required if the amount of each of the "weighed" glazes

requisite for the proper blending of each member, was weighed out direct. This was accordingly done.

THE FRITTS.

Opinion and custom differs widely as to what parts of the glaze should be incorporated in the fritted portion. As a rule, there is no cognizance taken of the solubility of the resultant fritt, nor any attempt to harmonize its chemical composition with that of the glaze. Since there is neither law nor general custom in this matter, the following rules were arbitrarily chosen:

1st. The fritt should constitute at least 50% by weight of the glaze.

2nd. Its oxygen ratio should be the same as that of the whole glaze.

3d. The fritt should contain (1) all of the alkaline salts including the feldspar; (2) all of the boracic acid and borax; (3) all but 0.05 equivalent of the required clay; (4) all but 0.10 equivalent of the total calcium oxide; (5) all of the free aluminum oxide; (6) only sufficient silica to maintain the required oxygen ratio. This left to be added raw to each of the "weighed" glazes the following:

0.25 Eqv. white lead

0.10 Eqv. whiting

0.05 Eqv. china clay

X Eqv. flint

The fritts were made in a crucible fritt furnace¹ fired by gas. The fritts when fused dropped from the crucible into cold water for granulation. It was found that all but two of the fritts were reasonably insoluble in water, but the comparatively ready solubility of the fritts belonging to weighed glazes No. 3 and 7 developed a belief that the fritts should not be run into water but rather out

¹Manufactured and donated to the Ceramic Department, University of Illinois, by W. D. Gates, American Terra Cotta and Ceramic Company, Chicago, Illinois.

onto a cold slab, refritted and then ground dry. Mr. J. F. Krehbiel suggested this plan, and has carried it out with good effect in the crystalline glaze experiments.

With the exception of the solubility of the two fritts cited, all eight fritts seemed to be normal. Their fluidity was sufficient to permit free flowage through the orifice of the crucible, and in no case was excessive heat or time required to affect the complete melting of the fritt.

Materials Used.

The following materials were used in this series of experiments:

C. P. Sodium Carbonate	Na_2CO_3
C. P. Potassium Nitrate	KNO_3
Whiting	CaCO_3
White Lead	$\text{Pb}(\text{OH})_2 \cdot 2\text{PbCO}_3$
Flint	SiO_2
Borax	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$
Boracic Acid (Flaky)	$\text{B}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$
Calcined Aluminum Oxide	Al_2O_3
Soda Feldspar. The analysis was as follows:	

	Per cents.
SiO_2	69.36
Al_2O_3	17.00
Fe_2O_3	0.53
CaO	0.62
MgO	0.88
K_2O	5.31
Na_2O	4.79

The molecular formula of the above is:

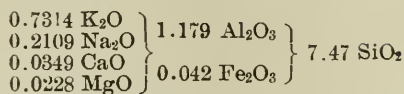
$$\left. \begin{array}{l} 0.385 \text{ K}_2\text{O} \\ 0.526 \text{ Na}_2\text{O} \\ 0.075 \text{ CaO} \\ 0.014 \text{ MgO} \end{array} \right\} \left. \begin{array}{l} 1.136 \text{ Al}_2\text{O}_3 \\ 0.023 \text{ Fe}_2\text{O}_3 \end{array} \right\} 7.884 \text{ SiO}_2$$

of which the combining weight is 669.6.

Potash Feldspar, from Brandywine Summit, Pennsylvania. The analysis was as follows:

	Per cents.
SiO_2	68.60
Al_2O_3	18.40
Fe_2O_3	0.54
CaO	0.30
MgO	0.14
K_2O	10.52
Na_2O	2.00
Moist.....	0.17

The molecular formula of which is:

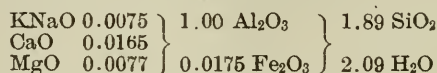


of which the combining weight is 663.79.

Georgia Kaolin. The analysis was as follows:

	Per cents.
SiO ₂	44.02
Al ₂ O ₃	39.51
Fe ₂ O ₃	1.09
CaO.....	0.36
MgO.....	0.12
KNaO.....	0.23
H ₂ O	14.60

The molecular formula of the above is:



of which the combining weight is 257.78.

PREPARATION OF THE GLAZES.

The fritts were wet-ground to pass freely a 100 mesh sieve, dried in newly-made plaster evaporating molds, and finally dried thoroughly by subjection to artificial heat.

As no water was poured off and thrown away, the only portion of the soluble materials in the fritts that was lost, was the trifle that entered the pores of the plaster evaporating molds. The uncertainty as to the absolute constitution of the fritts when finally ready for use was the only known irregularity in the whole experiment, and the writers believe that this is not very serious.

The eight "weighed" glazes were then weighed, wet-ground for a half hour, passed through a 100 mesh sieve, and dried in plaster evaporating molds.

Common RO $\left\{ \begin{array}{l} 0.194 \text{ Na}_2\text{O} \\ 0.191 \text{ K}_2\text{O} \\ 0.615 \text{ CaO} \end{array} \right.$

Table I. Chemical and Batch Formulæ of Fritts used in the eight weighed glazes.

Fritt Number.....	1		2		3		4		5		6		7		8	
	Eqv.	Batch	Eqv.	Batch	Eqv.	Batch	Eqv.	Batch	Eqv.	Batch	Eqv.	Batch	Eqv.	Batch	Eqv.	Batch
Equivalent Al_2O_3	0.077		0.615		0.077		0.615		0.077		0.615		0.077		0.615	
Equivalent SiO_2	0.683		1.86		1.23		2.845		1.5414		4.184		2.77		6.402	
Equivalent B_2O_3	0.364		0.657						0.8179		1.4786					
Combining Weight.	157.25		284.7		146.07		297.87		231.93		481.688		238.47		511.15	
Batch Formulæ																
Whiting	0.615	61.50	0.615	61.50	0.615	61.50	0.615	61.50	0.615	61.50	0.615	61.50	0.615	61.50	0.615	61.50
B. Feldspar.	0.065	43.15	0.249	165.14	0.065	43.15			0.065	43.15	0.261	173.25				
S. Feldspar.							0.235	157.08								
Potassium Nit.	0.143	28.89			0.143	28.89	0.055	11.11	0.143	28.89			0.068	45.53	0.368	246.55
Sod. Carbonate					0.18	51.48							0.165	33.33	0.049	9.90
China Clay											0.314	81.12	0.158	45.19		
Calc'd Alumina			0.3214	32.78			0.206	21.01							0.197	50.80
Flint.....	0.198	11.88			0.743	44.58			1.054	63.26	1.699	101.71	2.235	134.10	3.127	187.35
Boric Acid			0.36	44.64					0.455	56.37	1.202	149.05				
Borax	0.182	69.45	0.1485	56.73					0.182	69.45	0.188	52.72				

Table II. Chemical and Batch Formulae of the Eight "Weighed" Glazes.

$\left\{ \begin{array}{l} 0.126 \text{ Na}_2\text{O} \\ 0.124 \text{ K}_2\text{O} \\ 0.500 \text{ CaO} \\ 0.25 \text{ PbO} \end{array} \right\}$
 Common RO

	1		2		3		4		5		6		7		8	
Eqv. Al_2O_3	0.10		0.45		0.10		0.45		0.10		0.45		0.10		0.45	
Eqv. SiO_2	0.945		1.7091		0.13		2.35		2.127		3.85		2.925		5.2875	
Eqv. B_2O_3	0.2364		0.4273			0.552		0.96		
	Eqv.	Batch	Eqv.	Batch	Eqv.	Batch	Eqv.	Batch	Eqv.	Batch	Eqv.	Batch	Eqv.	Batch	Eqv.	Batch
Frits given in Table (I)....	0.65	102.06	0.65	185.06	0.65	94.80	0.65	193.62	0.65	144.03	0.65	313.10	0.65	154.77	0.65	332.25
Flint.....	0.4054	24.32	0.4054	24.32	0.4054	24.32	0.4054	24.32	0.4054	61.82	1.0304	61.82	1.0304	61.82	1.0304	61.82
China Clay...	0.05	12.90	0.05	12.90	0.05	12.90	0.05	12.90	0.05	12.90	0.05	12.90	0.05	12.90	0.05	12.90
White Lead...	0.25	64.50	0.25	64.50	0.25	64.50	0.25	64.50	0.25	64.50	0.25	64.50	0.25	64.50	0.25	64.50
Whiting.....	0.10	10.0	0.10	10.0	0.10	10.0	0.10	10.0	0.10	10.0	0.10	10.0	0.10	10.0	0.10	10.0

From the foregoing tables it is readily seen that the difference in composition and batch formulae lies wholly in the constitution of the fritt, except that each group contains progressively more and more free flint. For each group, however, there is a definite equivalent of free silica. The equal equivalent of fritt used in each case insures uniformity in the make-up of the several glazes, so that the difference in behavior of the glazes, one from another, can be said to lie wholly in their chemical constitution.

The actual formulae of the glazes, giving the Al_2O_3 , SiO_2 and B_2O_3 content of each, has been prepared in tabular form, but in order to facilitate close comparison between the composition of the glazes and their results on firing, the tables, marked Group I, Group II, etc., appear in connection with the results, instead of at this place.

BODY USED.

The body used in these experiments was furnished by the U. S. Encaustic Tile Co., of Indianapolis, Ind., through the courtesy of Mr. E. M. Ogle. It was delivered to the laboratories of the Ceramic Department of the University of Illinois in the shape of normally burned biscuit wall tile of apparently uniform density. The composition of the body as given by Mr. Ogle is as follows:

Ball Clay.....	40
China Clay.....	40
Cornwall Stone.....	20
Flint.....	22.5
	<hr/>
	122.5

PREPARATION OF THE TRIAL PIECES.

The question of how thick a layer of the glazes should be placed on the tile was considered seriously, for it was doubted if the difference between the behavior of the several glazes would be sufficiently exaggerated or emphasized if applied as thin as is the practice of the china and white ware potters, or even the wall tile manufacturers. Between

one-sixteenth and one-eighth of an inch was finally adopted as the thickness. The glazes that stand as "good" at this thickness will surely stand well when applied thinner, and those glazes which would have a tendency to craze or shiver would have that tendency increased by increased thickness, and thereby display their peculiarities almost at once after drawing from the kiln.

Five tile, marked in pencil with the proper group, series and member symbols, were thoroughly saturated with distilled water, placed side by side and the glaze paste applied over all five tile at once, with a spatula. After drying, the tiles were separated, fettled, and re-marked with a cobalt stain.

PLACING OF THE TRIAL PIECES.

The tiles were placed in the tile setters of such capacity that each held one whole series. The members of each series were placed in a setter in regular order, so that in case any of the tile should be stuck to the bottom of the setter, as a consequence of the running off of a portion of the excessively thick glaze, as happened in a few cases, each member of the series could be readily identified by its position in the setter. The identification of one specimen in each setter was, therefore, sufficient for the identification of the remaining members of the series.

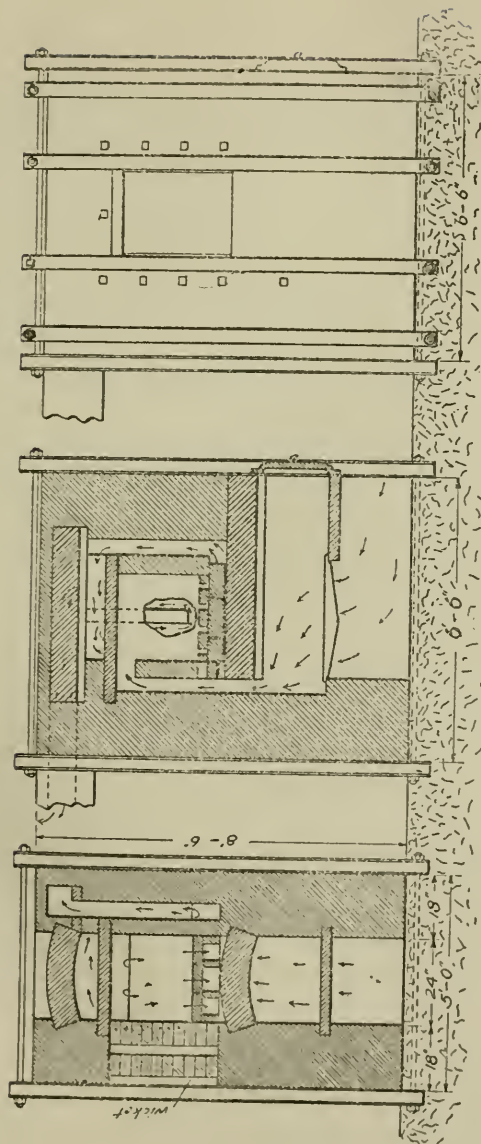
For nearly all burns above cone 010, the tile were placed on small wads with sufficient space between the tile and the setter bottom to permit of considerable running of the glaze without seriously cementing the tile to the setter.

BURNING OF THE GLAZES.

The glazes were burned in a side down-draft kiln designed by the senior writer, and built for the Ceramic Laboratory of the University of Illinois, as shown in Plate I.

TRANS. AM. CER. SOC. VOL. IX

PURDY AND FOX FIGURE 1



SIDE DOWN-DRAFT TRIAL KILN
IN USE IN THE CERAMIC DEPARTMENT OF THE
UNIVERSITY OF ILLINOIS
SCALE 0 1 2 3 FT.

This kiln was fired with coke, on the following time schedule:

- Cone 010 in 12 hours, 1 hour soaking, rapid cooling.
- Cone 05 in 14 hours, 1 hour soaking, rapid cooling.
- Cone 1 in 16 hours, 1 hour soaking, rapid cooling.
- Cone 5 in 18 hours, 1 hour soaking, rapid cooling.
- Cone 10 in 18 to 24 hours, 1 hour soaking, rapid cooling.

These heats were easily attained in the time allotted, with a very thin (3 inches) bed of live coals and an average of 20 to 30 minute firing periods. In fact, in all but the cone 10 burns, the raising of the heat was intentionally checked, so as to insure as close approximation to the above temperature schedule as possible.

In one of the cone 010 burns and one of the 05 burns, the kiln was "smoked" in the early part of the burn, which caused a deposition of carbon in the glazes that colored them black. This, however, did not injure the character or reduce the value of the results, for fortunately the smoked glazes were not in the series that matured at these temperatures.

Twenty-eight series or one-half of the entire 448 glazes were burned at a time, thus necessitating ten burns in all. The setters were placed in four bungs. In the first few burns, cones were placed near the top and bottom of each bung. In as much as the cones burned down equally in all eight positions, a fact that checked similar experience in this kiln in several previous burns on other forms of ware, sufficient confidence in the absolutely equal distribution of heat in all parts of the firing chamber was established, so that in the later burns only two and sometimes one set of cones was used in a burn.

RESULTS OF THE VARIOUS BURNS.

Group I.

A table of the compositions of the 64 glazes composing this group follows on page 27.

$$\text{RO} \left\{ \begin{array}{l} 0.120 \text{ Na}_2\text{O} \\ 0.124 \text{ K}_2\text{O} \\ 0.600 \text{ CaO} \\ 0.250 \text{ PbO} \end{array} \right.$$

Group I.

$$\text{OR} \left\{ \frac{0 \text{ in acids}}{0 \text{ in bases}} = \frac{2}{1} \right.$$

Glaze No.	Al ₂ O ₃ Eqv.	Series No. 1 Ratio 1:0.25		Series No. 2 Ratio 1:0.20		Series No. 3 Ratio 1:0.17		Series No. 4 Ratio 1:0.13		Series No. 5 Ratio 1:0.09		Series No. 6 Ratio 1:0.06		Series No. 7 Ratio 1:0.01		Series No. 8 Ratio 1:0.00	
		SiO ₂	B ₂ O ₃	SiO ₂	B ₂ O ₃	SiO ₂	B ₂ O ₃	SiO ₂	B ₂ O ₃	SiO ₂	B ₂ O ₃	SiO ₂	B ₂ O ₃	SiO ₂	B ₂ O ₃	SiO ₂	B ₂ O ₃
a	0 10	0.9454	0.2363	1.0000	0.2000	1.0358	0.1761	1.0878	0.1414	1.1454	0.1031	1.2093	0.0605	1.2808	0.0128	1.30
b	0 15	1.0545	0.2636	1.1153	0.2231	1.1554	0.1964	1.2134	0.1577	1.2775	0.1149	1.3488	0.0674	1.4286	0.0143	1.45
c	0 20	1.1636	0.2909	1.2308	0.2461	1.2749	0.2167	1.3389	0.1741	1.4097	0.1269	1.4884	0.0744	1.5764	0.0157	1.60
d	0 25	1.2727	0.3181	1.3461	0.2690	1.3944	0.2371	1.4644	0.1904	1.5418	0.1387	1.6279	0.0814	1.7241	0.0172	1.75
e	0 30	1.3818	0.3454	1.4615	0.2930	1.5139	0.2574	1.5900	0.2067	1.6740	0.1506	1.7674	0.0884	1.8719	0.0187	1.90
f	0 35	1.4909	0.3727	1.5769	0.3154	1.6334	0.2777	1.7155	0.2230	1.8061	0.1625	1.9070	0.0953	2.0197	0.0202	2.05
g	0 40	1.5999	0.3999	1.6923	0.3385	1.7529	0.2980	1.8410	0.2393	1.9383	0.1744	2.0465	0.1023	2.1675	0.0216	2.20
h	0 45	1.7091	0.4273	1.8077	0.3615	1.8725	0.3183	1.9665	0.2556	2.0704	0.1863	2.1860	0.1093	2.3153	0.0232	2.35
Variation in Silica per 0.05 eqv. Al ₂ O ₃		0 1090909		0 1153846		0 1195219		0 125523		0 1321585		0 1395348		0 147783		0 150	
Variation in B ₂ O ₃ per 0.05 eqv. Al ₂ O ₃		0 0273727		0 0230769		0 0203187		0 01631769		0 0118943		0 0069767		0 001478		

Fired at Cone 010.

Series 1. All fused to glasses; none attacked the body.

Members a, b, c, devitrified and badly crazed in both thin and thick places.

Member d slightly devitrified, crazed, good gloss on most of surface.

Members e, g, f, h, good glazes where thin, but have small pin holes on surface where thick. Pin-holing increases as B_2O_3 decreases. Crazed whether thick or thin.

Series 2, 3, 4. All devitrified and all effloresced. Devitrification decreases with increase of Al_2O_3 .

Series 5, 6, 7. Are like 2, 3 and 4 except that with low Al_2O_3 crackling or separation of the glaze begins in series 5 and increases progressively until it is the most manifest in series 8.

Series 8. Is very badly crackled, the glaze patches exhibiting a vitreous sheen.

Summary of Group I at Cone 010.

- (1) The Eqv. content of Al_2O_3 with which the best glazes are developed at this temperature ranges from 0.30 to 0.40, with the ratio of SiO_2 to B_2O_3 1:0.25.
- (2) Devitrification decreases with increase of Al_2O_3 and the decrease of B_2O_3 .
- (3) Efflorescence was general in whole series.

Fired at Cone 05.

Series 1. Devitrification is less at this temperature than at cone 010. Crazing is finer meshed in the glazes which have lower equivalent of Al_2O_3 . Crazing more pronounced in all glazes at this temperature than at 010.

Series 2, 3. All glazes of these two series are dimmed less at this temperature than they were at 010.

The most fusible member of both series is "e," having an Al_2O_3 content of 0.30 Eqv. In both series, it has but a trace of dimness.

The members f, g, h, in both series show graded increase in refractoriness.

Series 4, 5, 6. These three series exhibit a most peculiar appearance in that they have passed from what appeared to be devitrification in the cone 010 burn, to a blistered dull surface due to the boiling that precedes quiet fusion.

Members e and f seem to be the most fusible of these series.

Series 7. Members a, b, c, present same crackled appearance as at cone 010.

Members d, e, f, are devitrified, matt-like in appearance; e being a beautiful matt, but badly crazed.

Series 8. Carbonized badly, but are apparently more fused than at cone 010.

Summary of Group I at Cone 05.

- (1) Good glazes having an Al_2O_3 equivalent of 0.3 to 0.4 occur in Series 1, 2 and 3.
- (2) Devitrification decreases with increase of Al_2O_3 and decrease of B_2O_3 .
- (3) None effloresced.
- (4) Fair matt surface occurs in Series 7 with 0.30 Eqv. Al_2O_3 .
- (5) Crazing is more pronounced in cone 05 burn than at 010.
- (6) Glaze e, series 1, has the longest range so far developed, being good at 010 and at 05.
- (7) Glazes f and g are very nearly matured at 010 and fully so at 05.
- (8) Crazing decreases with increase of Al_2O_3 and changes from fine mesh to long hair lines.

Fired at Cone 1.

Series 1. Members a, b, c, d have good gloss; are perfectly matured; crazed in fine meshes and have eaten into the body, glaze "a" being the worst in this respect.

Members e, f, g are good, well matured glazes; "e" is considerably crazed but the craze lines are long and some distance apart; "f" is less crazed and "g" has but one craze line.

Member g is not quite matured.

What is stated in the discussion of the 05 burn in reference to the decrease in devitrification phenomena of series 1, seems to find confirmation in the cone 1 burn, for the glazes that were badly devitrified at 010 were less so at 05, and not at all at cone 1, but at cone 1 the edges of the tile are eaten away by the glaze, and this eating away of the edges decreases as the glaze increases in Al_2O_3 . This lends support to the doctrine (1) that Al_2O_3 counteracts devitrification; (2) that glazes having the acidity of this group must contain at least 0.30 Eqv. of Al_2O_3 to satisfy the acid content.

This series brings out another very significant fact that has been noted in many other isolated examples, to-wit: that when the glaze is compelled to feed upon the body to gain the Al_2O_3 required to make a perfect glaze, fine mesh crazing is sure to follow. This increase in crazing with increase of Al_2O_3 does not accord with Seger's law in which the introduction of bases of high molecular weight is credited with power to decrease crazing. But, as will be noted later, Seger's law in regard to decrease of crazing with increase of Al_2O_3 does hold true when the original content of Al_2O_3 of the glaze is considered. Increase in Al_2O_3 by eating into the body increases rather than decreases crazing.

No scumming or devitrification was apparent in any member of this series.

Series 2, 3 and 4. The members of these series resemble series 1 in every respect save that of maturity. In series 1, all members but h are fully matured, while in series 2, 3 and 4 g is likewise unmatured.

The fine-mesh crazing in a, b, c, d, and to some extent in e, is shown in these series as in series 1, but the

members f, g, h, are freer from crazing as the B_2O_3 decreases, i. e. progressively from series 1 to series 4 inclusive. This would seem to be rather significant in view of the fact that all the succeeding series have dimmed surfaces which resemble devitrification more than immaturity.

Series 5 and 6. Not a single member of these series is matured.

Members a, b, c, d, and e show progressive decrease in dimness (probably devitrification) with increase of Al_2O_3 . None have eaten into the body.

Series 6. Members a and b are smooth, devitrified and fine-mesh crazed.

Other members are in the "boiling" stage. Member d with 0.25 Al_2O_3 exhibits this more than the others.

Series 7. All members of this series cover the tile perfectly showing that increase of heat treatment from cone 05 to 1 has been sufficient to cause these glazes to flow enough to pass from a crackeled condition to a perfect coating of glass.

Series 8. All members are dim with slight evidence of devitrification.

All are crazed in fairly fine meshes.

Summary of Group I at Cone 1.

(1) Good Glasses developed at this heat are as follows:

Series 1 a to h inclusive.

Series 2 a to g inclusive.

Series 3 a to g inclusive.

Series 4 a to g inclusive.

(2) Good glazes, having only hair line crazes, or none at all and being free from pinholes.

Series 1 e, f, g, h.

Series 2 e, f, g.

Series 3 f, g.

Series 4 f, g.

- (3) Glazes d, e, f, series 7, that exhibited good matt texture at cone 05 were "boiling" at cone 1, showing that at cone 05 their matt surface was due entirely to immaturity.
- (4) At this temperature, eating into the body decreases with decrease in B_2O_3 and increase in Al_2O_3 .
- (5) Crazeing passes from fine mesh to total absence with increase to Al_2O_3 . With low Al_2O_3 (0.1 to 0.25 and 0.3 inclusive) decrease in B_2O_3 does not seem to affect the character or amount of crazeing, but with higher Al_2O_3 there is shown a progressive decrease in crazeing with decrease of B_2O_3 . This would indicate at least four important facts.
 - (a) Increase in Al_2O_3 decreases crazeing.
 - (b) Increase of SiO_2 , retaining constant oxygen ratio, likewise decreases crazeing, but
 - (c) Al_2O_3 is a more powerful factor than SiO_2 in checking crazeing at this heat treatment and oxygen ratio.
 - (d) The facts noted in a and c only hold true when the original Al_2O_3 content is considered. When the glaze is compelled to borrow Al_2O_3 from the body, a strain is established that increases crazeing in proportion to the extent to which the glaze has attacked the body.

On looking down into the thicker portions of the glazes which have eaten into the body, and which exhibit this fine mesh crazeing to the greatest degree, there appears to be a separation or splitting between portions of the glazes next to the body and those nearer the surface. It is quite evident from this, that the portion of glaze in contact with the body is of a different composition from that near the surface. There cannot be ready diffusion of materials in glazes of this oxygen ratio, even when relatively high in B_2O_3 . From the fact that the glazes lowest in Al_2O_3 have eaten into the body most, exhibit fine-mesh crazeing to

the greatest degree, and show a separation between the portion of glaze contiguous to the body and that above, it is concluded that this fine-mesh crazing is due more largely to extraction of Al_2O_3 than to the extraction of SiO_2 from the body, which owing to its viscosity, diffuses very reluctantly, and further, that this fine-mesh crazing increases with the increase of Al_2O_3 so obtained by the glaze.

(6) Devitrification extends only from series 5 to 8 inclusive, or over a proportional range of SiO_2 B_2O_3 from 1:0.9 to 1:0.

(7) It is indeed a most surprising fact that with the oxygen ratio of 2, which is best suited to the development of good glossy raw-lead glazes free from boracic acid, there should not be developed a good glass, when a portion of the glaze is fritted, until the ratio of silica to boracic acid has been raised to at least 1:0.13 and then only within a very narrow range of variation in Al_2O_3 . Indeed, as will be seen in the study of this same group at cone 5, fritted glazes having an oxygen ratio of 2 have a heat range that is limited to but a slight variation from cone 1 until the ratio of SiO_2 to B_2O_3 has reached 1:0.2. Even at the SiO_2 — B_2O_3 ratio of 1:2.0 at least cone 1 is required to mature the glaze, and at cone 5 it has withstood its maximum heat treatment.

On the other hand, when the boracic acid has been increased until the ratio of SiO_2 to B_2O_3 stands at 1:0.25 there seems to be established a degree of fusibility and a restraint against devitrification that permits of heat treatment ranging from cone 010 to at least cone 5 inclusive, provided that Al_2O_3 content originally incorporated in the glaze is at least equal to 0.3 or 0.4 equivalents.

Fired at Cone 5.

Series 1, 2, 3 and 4. All glazes are crazed, fine-mesh crazing the most pronounced with low Al_2O_3 and increasing B_2O_3 . Glazes that were not crazed at Cone 1 are crazed at Cone 5 in long hair lines.

Except for crazing, the following are good glazes:

Series 1 d, e, f, g, h.

Series 2 c, d, e, f, g, h.

Series 3 none.

Series 4 f, g, h.

In series 1, fine-mesh crazing is about as it was in same series at Cone 1, except in case of member d, which has flowed and run off the tile, leaving only a comparatively thin coating of glaze. While the body shows evidence of having been attacked to some extent, the glaze is coarser crazed and freer from horizontal crazing than member e, which is thicker. This fact suggests three things.

(1) Fine-mesh crazing can be decreased by decrease in thickness of glaze, thus permitting equal diffusion of the Al_2O_3 obtained from the body throughout the whole mass.

(2) The body will be attacked less the thinner the glaze.

(3) That fine-mesh crazing is due almost entirely to the unequal coefficient of expansion and contraction of the upper and lower portion of the glaze layer.

In all of the series of this group, the fine-mesh crazing is exhibited in glazes which at cone 05 were either free from crazing or were crazed only in hair lines. Members g and h in all series are still free from this fine-mesh crazing, but it is evident that as the heat increases in intensity, even though not in length of time, the glazes originally higher in Al_2O_3 are beginning to attack the body, causing tension between the upper and lower portions of the glaze, that causes either actual or incipient horizontal as well as vertical crazing and as a consequence, fine-mesh phenomena; and that in the glazes originally low in Al_2O_3 the alumina incorporated from the body is much more thoroughly diffused, causing, as a consequence, a de-

crease in the fine-mesh crazing over that shown with less intense heat. These facts are very clearly shown at cone 10, where the glazes having the finest mesh crazing were originally highest in Al_2O_3 and at lower heats, in some cases, are entirely free from crazing.

Series 5, 6, 7 and 8. Devitrification is now shown only in members a, b and c of series 6 and 7, and in all members of series 8. None are free from crazing. Members having highest original content of Al_2O_3 exhibit pin-holing. No glazes of promise shown in any portion of these series.

Summary of Group I at Cone 5 will be included with the summary of the facts deduced from the Cone 10 burn.

Fired at Cone 10.

All members of every series of Group I at this heat treatment are crazed in fine meshes.

In series 1, member a is not so very finely crazed, but the fine craze meshes increase regularly from a up to f, which had originally 0.35 Eqv. Al_2O_3 and then decrease slightly from member f to h.

In series 2, member f again marks the point of maximum fine-mesh crazing.

From series 2 to 8, the area of maximum fine-mesh crazing increases until in series 8, every member is crazed in exceedingly fine meshes.

Every glaze ate into the body considerably, those showing maximum fine-mesh crazing being no worse in this respect than those showing this feature in a less degree.

Summary of Group I at Cones 5 and 10.

(1) It is quite evident that for fritted glazes of this oxygen ratio and RO, on this body, cone 5 is beyond the

maximum limit of temperature, for all the glazes are more or less crazed in fine meshes. On a body that would not give up any of its constituent parts to the glaze, or if the glazes were dipped as thin as is the practice in the white ware industry, many of these glazes may have a heat range that would include at least cone 5 if not cone 10. The extreme thickness at which these glazes were applied, permitted the formation of two strata, the one next to the body containing without a doubt additional Al_2O_3 , while the upper strata was not altered materially in composition, except by the normal volatilization of B_2O_3 and alkalis.

Conclusion on Group I.

1. The good glazes developed at the several temperatures are noted in the following table. The glazes which have a question mark beside them are good glasses, which might have been good glazes if they had been applied thin enough to prevent the formation of two strata in the glaze layer, thus causing fine-mesh crazing. Normal crazing is not taken into account in designating a glaze as good.

Series	Cone 010	Cone 05	Cone 1	Cone 5	Cone 10
1	e f g h	d? e? f g h	b? c? d? e f g h	b? c? d? e? f g h	(a to h)?
2		e? f	b? c? d? e f g	b? c? d? e? f? g?	(a to h)?
3		e f	b? c? d? e f g	(a to g)?	(a to h)?
4			c? d? e f g	(a to g)?	(b to h)?
5				f? g?	(b to c)?
6				f? g?	none
7				e? f? g?	none
8					(b to f)?

2. Series 8 of this group demonstrates the fact which was stated by the senior writer, in 1904; viz., a fritted glaze must have a higher oxygen ratio than 1:2 or that normally used in raw lead glazes. True, good glazes with a fair temperature range were developed in this group, but they required the maximum content of B_2O_3 .

3. Fine-mesh crazing appears to be due to unequal dissemination of constituents taken from the body, and is more pronounced at the low temperatures in those glazes that are lowest in Al_2O_3 irrespective of their B_2O_3 content, and as the intensity of the heat increases, fine-mesh crazing decreases in the glazes low in Al_2O_3 , in consequence of the compounds extracted from the body, and progresses steadily with increase in intensity of heat until the glazes having an Al_2O_3 content of 0.3 to 0.4 Eqv. that were perfect at the lower heat treatment because crazed in fine meshes at the higher heat treatment.

4. Devitrification decreases as the Al_2O_3 increases, either as originally added or taken from the body.

Group II.

A table of the compositions of the 64 glazes composing this group follows on page 38.

$$\text{OR} \left\{ \frac{0 \text{ in acids}}{0 \text{ in bases}} = \frac{2.5}{1} \right.$$

Group II.

$$\text{RO} \left\{ \begin{array}{l} 0.126 \text{ Na}_2\text{O} \\ 0.124 \text{ K}_2\text{O} \\ 0.500 \text{ CaO} \\ 0.250 \text{ PbO} \end{array} \right.$$

Glaze No.	Al ₂ O ₃ Eqv.	Series No. 1 Ratio 1:0.25		Series No. 2 Ratio 1:0.20		Series No. 3 Ratio 1:0.17		Series No. 4 Ratio 1:0.13		Series No. 5 Ratio 1:0.09		Series No. 6 Ratio 1:0.05		Series No. 7 Ratio 1:0.01		Series No. 8 Ratio 1:0.00	
		SiO ₂	B ₂ O ₃	SiO ₂	B ₂ O ₃	SiO ₂	B ₂ O ₃	SiO ₂	B ₂ O ₃	SiO ₂	B ₂ O ₃	SiO ₂	B ₂ O ₃	SiO ₂	B ₂ O ₃	SiO ₂	B ₂ O ₃
a	0.10	1.1818	0.2955	1.2500	0.2500	1.2948	0.2201	1.3598	0.1788	1.4317	0.1289	1.5116	0.0756	1.6009	0.0160	1.6250
b	0.15	1.3182	0.3295	1.3942	0.2788	1.4412	0.2455	1.5167	0.1972	1.5969	0.1437	1.6860	0.0843	1.7857	0.0179	1.8125
c	0.20	1.4545	0.3636	1.5385	0.3077	1.5936	0.2709	1.6736	0.2176	1.7621	0.1586	1.8605	0.0930	1.9705	0.0197	2.0000
d	0.25	1.5909	0.3977	1.6827	0.3365	1.7430	0.2963	1.8305	0.2380	1.9273	0.1736	2.0389	0.1017	2.1553	0.0216	2.1875
e	0.30	1.7273	0.4318	1.8269	0.3654	1.8924	0.3217	1.9874	0.2584	2.0925	0.1884	2.2133	0.1105	2.3401	0.0234	2.3750
f	0.35	1.8636	0.4659	1.9712	0.3942	2.0418	0.3471	2.1443	0.2758	2.2577	0.2033	2.3877	0.1192	2.5249	0.0253	2.5625
g	0.40	2.0000	0.5000	2.1154	0.4230	2.1912	0.3725	2.3012	0.2992	2.4229	0.2182	2.5621	0.1279	2.7097	0.0271	2.7500
h	0.45	2.1364	0.5341	2.2596	0.4519	2.3406	0.3979	2.4582	0.3196	2.5881	0.2330	2.7365	0.1366	2.8945	0.0290	2.9375
Variation in SiO ₂ per 0.05 eqv. of Al ₂ O ₃		0.1363637		0.144230		0.14940203		0.156901		0.165148		0.174418		0.1848		0.1875	
Variation in B ₂ O ₃ per 0.05 eqv. of Al ₂ O ₃		0.0340909		0.028846		0.0253954		0.020397		0.0148673		0.008721		0.00185		

Fired at Cone 010.

Series 1-8 1. All were heavily impregnated with carbon, so that but little can be said of the behavior of the glazes of this group at 010.

2. Members d, e and f, of series 1, 2, 3 and 4, seem to be the most fusible.

Fired at Cone 05.

- (1) Members d and e of series 1, were the only two good glazes developed with this heat treatment and thickness of glaze.

The entire group had evidently been subjected, in burning, to the influence of carbon, shortly after members d and e had been fused into perfect glasses, for the less fusible glazes show either an undulating or a pimply surface, where they are thick, on account of the expulsion of CO or CO₂ generated by the combustion of the carbon, but were smooth, well developed glazes where thin.

- (2) The glazes retaining the carbon to the end of the burn are to the left of a line drawn diagonally from member a in series 1 to member h in series 8. This according to Seger¹ demonstrated that the glazes to the right of this diagonal line were nearly formed into glasses at the time that the kiln was "smoked." Further, those glazes which were fairly well developed at cone 010 and are good at cone 1, show least of this undulating and pimply surface.

From these facts at least three conclusions can be drawn.

(a) The most fusible mixture in series 1, 2 and 3 is that with 0.30 Eqv. of Al₂O₃.

(b) In series 4, the most fusible mixture contains 0.35 Eqv. of Al₂O₃; in series 5 and 6, 0.45 Eqv. of Al₂O₃.

¹Collected Writings of Herman A. Seger. Amer. Cer. Soc. trans. Vol. II, p. 592.

(3) Judging from the appearance of the glaze where thin, and the relative degree of maturity at cone 010 and cone 1, the following glazes would have been well developed had they not been "smoked."

Series 1 d, e, f, g, h ?

Series 2 c, ? d, ? e, f, g ?

Series 3 c ? d ? e, f, g ?

Series 4 e ? f ?

Series 5 0.

Dimness of surface is equally pronounced in this group when either Al_2O_3 is low and B_2O_3 high, or Al_2O_3 is high and B_2O_3 low.

Fired at Cone 1.

- (1) The more refractory glazes of the first four series exhibited surface pinholing or pitting, especially where the glaze is thick. The surface pinholing could readily be taken as indicating an over-burned condition, but such could not be the case, for they show no indication of being over-burned at cone 5.
- (2) Members of series 4, 5 and 6 are likewise pinholed, but owing to their being less fusible than the members of the first three series, most of the trial pieces appear to have a narrow border of normally fused glaze surrounding a more boiled and pitted patch in the center.
- (3) Series 7 and 8 are slightly blackened by carbon, showing that the whole group had been smoked.

These three facts suggest that:

(a) Pinholing, which appears at times when every condition seems to be normal, may be traced largely to the carbon which was entrapped when the glaze was almost matured, the combustion of which produced gas that developed blisters, or blibs, which finally bursted, forming small pits or pin holes. These pinholes differ somewhat from the blisters due to over-burning, in that the latter extend much deeper into the glaze layer, and are frequently much larger in diameter.

(b) It cannot as yet be determined whether the carbon reduced the lead, thus altering its chemical activity in respect to the boro-silicate formation that is taking place, or whether the presence of carbon and the consequent carbonic gases make the glaze more viscous. There is evidence in this group that might be taken to substantiate either claim. The essential fact is that if one portion of a glaze has been smoked, and another portion not smoked, the former will have every appearance of being over-fired save that of the nature of the pinholes, while the portion not smoked may be a normally developed glaze.

- (4) The glazes of group II, which either are good, or would have developed into good glazes at cone 1 were it not for their having been smoked, are as follows:

Series 1 c, d, e, f, g, h.

Series 2 c, d, e, f, g, h.

Series 3 b, c, d, e, f, g, h.

Series 4 b? c? d, e, f? g?

Series 5 e? f? g.

- (5) Devitrification and fine-mesh crazing are developed in this group at cone 1 under the same conditions that were noted in case of the first group. The essential difference in the occurrence of these effects is that 1st, fine-mesh crazing is confined to glazes having a lower equivalent of Al_2O_3 than is the case in group 1; 2nd, devitrification is a trifle less pronounced in this group at cone 1 than it was in Group I at the same heat treatment.

Fired at Cone 5.

Series 1, 2, 3, 4, (1) Fine-mesh crazing occurs to the right of a line drawn from members e of Series 1 to member a Series 5.

(2) Attack on body by the glaze is evident only in the glazes which are crazed in fine meshes.

(3) In these series at cone 5 as in every other instance so far noted, members e and f (0.30-0.35

Al_2O_3) are the best matured and freest from defects.

(4) Good glazes, including only those which are free from fine-mesh crazing and are well matured, are:

Series 1 e, f, g, h.

Series 2 d, e, f, g, h.

Series 3 d, e, f, g, h.

Series 4 c, d, e, f, g, h.

Series 5 c, d, e, f, g, h.

Series 6, 7, 8. (1) Devitrification is shown in these series to a less extent than in similar series of Group I at the same temperature.

(2) Members e and f of Series 6 and 7 are fair glazes but contain matter in suspension.

(3) Series 8 at this higher oxygen ratio is further matured than the same series of Group I, thus emphasizing the fact that when a portion of a raw lead glaze is fritted, the oxygen ratio of the glaze must be more than 1:2.

Fired at Cone 10.

The appearance of the glazes of Group I and Group II at this temperature is almost identical. The statements made concerning Group I hold true of Group II at cone 10, except perhaps that the crazing is not quite so fine meshed in Group II.

Conclusions on Group II.

The good glazes developed at the several heats are shown in the following table. Those glazes having a question mark beside them, it is believed, would have developed into good glazes had they not been reduced or blackened by deposition of carbon in firing.

Series	Cone 010	Cone 05	Cone 1	Cone 5	Cone 10
1	e? f?	d e f g h?	c d e f g h	d e f g h	(a to h)?
2	e? f?	d? e f g?	c d e f g h	c d e f g h	(a to h)?
3	e? f?	d? e f g?	c d e f g h	c d e f g h	(a to g)?
4			c? d e f? g?	c d e f g h	(a to f)?
5			e? f?	c d e f g h	overburned
6				c? d? e? f g h?	overburned
7				f g? h?	overburned
8				h?	overburned

2. The glazes having an oxygen ratio of 1:2.5 show a longer heat range than those having a ratio of 1:2.0.

3. Crazing in fine meshes is decreasing in intensity with increase in oxygen ratio.

4. At heat treatments below cone 5, fine-mesh crazing is greatest with lowest Al_2O_3 content, but as the temperature increases from cone 5 to cone 10, this crazing reaches its maximum with higher and higher content of Al_2O_3 . It is more pronounced where B_2O_3 is present in the largest amounts. Both of these facts agree with those observed in Group I, and in both cases the conclusion that fine-mesh crazing is due largely to the Al_2O_3 extracted from the body and diffused throughout the glaze magma very slowly, seems to be fully justified.

5. It is rather difficult on first thought to harmonize conclusions 3 and 4, for in either group, when considered separately, increase in the Al_2O_3 originally added, counteracts a tendency to craze in fine meshes, and when Groups I and II are compared one with another, it is seen that increased acidity in the original composition of the glaze also counteracts fine-mesh crazing as did increased Al_2O_3 . Referring to the description of the fine-mesh crazing in Group I at cones 5 and 10, it is seen that members a and b, which exhibited it the most at the lower heats, were the most free from it at the higher heats. Complete saturation by Al_2O_3 in these members at the high heats and incomplete diffusion of Al_2O_3 in the members higher in "original" content of Al_2O_3 where viscosity is the greatest, is offered as the explanation of this phenomenon. Increased acidity, up to a given degree, decreases viscosity and increases ease of diffusion, so that in the case of Group II it would be expected that the Al_2O_3 taken from the body would be more readily diffused throughout the glaze magma, thus decreasing the liability to the formation in the glaze of two strata of different composition.

6. From the fifth conclusion it is seen that in this

case, increase in acid does not increase the viscosity of the glaze, but on the contrary, it actually makes the glaze less viscous. The general assertion, therefore, that SiO_2 added to a fritted glaze makes the glaze more viscous is not true at these lower oxygen ratios.

7. The smoking of the burns at cone 010, 05. and 1 suggested a cause for the appearance of pinholes in glazes that are normally free from them. Mr. Gray at the Boston meeting of the society made a formal inquiry concerning this phenomenon, stating that it occurs very freakishly, first in one part of the kiln, then in another, and often not appearing for several burns at a time.

Those who have attempted to make raw-lead feldspar glazes on a commercial scale have learned that for a given temperature the glaze cannot vary much in composition without the formation of these pinholes or blisters, as they are sometimes called, appearing frequently and in the most unexpected places.

The condition of the glazes of Group II at the three lower temperatures suggests that if carbon is deposited on glazes when they are just in the fritting state and is burned out while the glaze is maturing, the carbonic oxide gas generated, not only forms miniature craters when it escapes, but also reduces the lead, and perhaps thereby alters the nature of the compounds formed in the matrix, making the glaze more viscous and thus preventing the healing over of the craters by flowage of the glaze.

In ordinary firing, the temperature is raised most rapidly just before and during the time that the glaze ingredients are passing from the sintering through the fritting stages. The glazes that have progressed furthest in the glass-forming stage are least affected by carbon, and hence exhibit fewer pinholes when matured. For this reason, Cornwall stone glazes are freer from pinholes than feldspar glazes.

Group III.

A table of the compositions of the 64 glazes composing this group follows on page 45.

$$\text{RO} \left\{ \begin{array}{l} 0.126 \text{ Na}_2\text{O} \\ 0.124 \text{ K}_2\text{O} \\ 0.500 \text{ CaO} \\ 0.250 \text{ PbO} \end{array} \right.$$

Group III.

$$\text{OR} \left\{ \frac{0 \text{ in acids}}{0 \text{ in bases}} = \frac{3.0}{1} \right.$$

Glaze No.	Al ₂ O ₃ Eqv.	Series No. 1 Ratio 1:0.25		Series No. 2 Ratio 1:0.20		Series No. 3 Ratio 1:0.17		Series No. 4 Ratio 1:0.13		Series No. 5 Ratio 1:0.09		Series No. 6 Ratio 1:0.05		Series No. 7 Ratio 1:0.01		Series No. 8 Ratio 1:0.00	
		SiO ₂	B ₂ O ₃	SiO ₂	B ₂ O ₃	SiO ₂	B ₂ O ₃	SiO ₂	B ₂ O ₃	SiO ₂	B ₂ O ₃	SiO ₂	B ₂ O ₃	SiO ₂	B ₂ O ₃	SiO ₂	B ₂ O ₃
a	0.10	1.4132	0.3546	1.5000	0.3000	1.5535	0.2641	1.6318	0.2121	1.7181	0.1545	1.8140	0.0907	1.9212	0.0192	1.9500
b	0.15	1.5818	0.3955	1.6731	0.3346	1.7331	0.2946	1.8201	0.2366	1.9163	0.1725	2.0233	0.1012	2.1429	0.0214	2.1750
c	0.20	1.7454	0.4364	1.8462	0.3692	1.9123	0.3251	2.0084	0.2611	2.1145	0.1903	2.2326	0.1116	2.3645	0.0236	2.4000
d	0.25	1.9090	0.4773	2.0192	0.4038	2.0916	0.3558	2.1967	0.2856	2.3128	0.2082	2.4419	0.1221	2.5862	0.0258	2.6250
e	0.30	2.0726	0.5182	2.1923	0.4384	2.2709	0.3801	2.3850	0.3101	2.5110	0.2260	2.6512	0.1326	2.8079	0.0281	2.8500
f	0.35	2.2362	0.5591	2.3654	0.4731	2.4502	0.4165	2.5732	0.3345	2.7093	0.2438	2.8605	0.1430	3.0295	0.0303	3.0750
g	0.40	2.3998	0.6000	2.5385	0.5077	2.6295	0.4470	2.7615	0.3590	2.9075	0.2617	3.0698	0.1535	3.2512	0.0325	3.3000
h	0.45	2.5634	0.6409	2.7115	0.5423	2.8087	0.4775	2.9498	0.3835	3.1057	0.2795	3.2791	0.1640	3.4729	0.0347	3.5250
Variation in SiO ₂ per 0.05 eqv. of Al ₂ O ₃		0.1636		0.17307		0.17928		0.18829		0.19824		0.20930		0.22167		0.225	
Variation in B ₂ O ₃ per 0.05 eqv. Al ₂ O ₃		0.0409		0.0346		0.01648		0.02448		0.017842		0.010465		0.022167		

Fired at Cone 010.

This group was badly carbonized in this heat treatment, so that little can be said in regard to it.

Series 1, 2, 3. From the fact that Series 1 of Group I and series 1 of Group IV developed glasses a few of which were fair glazes, it is safe to assume that similar results could be expected from the same series of this Group.

Series 1 and 2 are alike in that the glazes are greyish and badly boiled and honey-combed. The carbon has either delayed the glass formation or has not permitted it to come to a "quiet" fusion. While the latter case may be true in part, it is believed that the delay in formation of a glassy structure is probably the real effect of the presence and burning out of carbon as shown in these series.

Series 4, 5, 6, 7, 8. These series are not "boiled" but grade regularly from fused masses in Series 4, down to porous grey coatings in Series 8.

There is one new fact shown in this series which is not borne out in any other group or temperature, but which is very suggestive. In series 4, 5, 6, 7, 8, the glazes lowest in Al_2O_3 , i. e. glazes a, b, and c, are fused, while the glazes having 0.30-40 Eqv. Al_2O_3 are porous. In series 1, 2 and 3 at this heat treatment it is the glazes that have this higher equivalent of Al_2O_3 that appear to be the most matured. In all other instances noted, these same glazes would be well matured when those lower in Al_2O_3 had not yet fully formed into a matured glaze. Can it be then, that the glazes lowest in Al_2O_3 at this oxygen ratio begin fusion earliest but do not complete their maturity as early as those in which the Al_2O_3 is higher, while at lower oxygen ratio it is the glazes higher in Al_2O_3 that fuse earliest?

Fired at Cone 05.

Series 1, 2, 3. Members a, b, c, d, e, of these series are well matured glazes.

Member f in each case appears well matured, but is pitted in a way that gives rise to a suspicion that these series had been slightly smoked.

Members g and h have more pronounced "smoke defects" than f, but the appearance of these members does not warrant a statement concerning their maturity at this heat.

Series 4, 5, 6. Are all very much alike in that members a, b, and c are devitrified masses.

Series 7, 8. Are stony in appearance and the lower members slightly effloresced.

Summary of Group III at Cone 05.

The following are considered as being "good" at this heat:

Series 1 a, b, c, d, e, f? g?

Series 2 a, b, c, d, e, f g?

Series 3 a, b, c, d, e.

Fired at Cone 1.

Series 1, 2, 3. Members a, b, c, d, e, f of these series have fine gloss, and are in the main free from crazing and pinholing.

Member h of each of these series contains suspended matter that resembles a flocculent precipitate.

Otherwise member h gives some promise as a glaze.

Series 4. Other than pin-holing and undissolved material where the glazes are thickest, members a, b, c, d, e, f and possibly g are well fused and matured.

Series 6, 7. Members a, b, and c are just passing from the devitrified to the glassy state. The remaining members of these series are semi-glassy, but with poor evidence of good glass possibilities.

Series 8. Members a and b are devitrified, while the remaining members show a fair enamel gloss.

Summary of Group III at Cone 1.

The following glazes are considered as being good at this heat:

Series 1	a, b, c, d, e, f, g.
Series 2	a, b, c, d, e, f, g?
Series 3	a, b, c, d, e, f, g.
Series 4	a, b, c, d, e, f, g?
Series 5	e? f?
Series 6	—

Fired at Cone 5.

Series 1, 2, 3, 4. (1) All members of these series are well matured glazes, and free from all defects, except that of crazing in the lower members.

(2) It is with this heat treatment that glazes of this group first show fine-mesh crazing.

Series 1, members a and b, are crazed more than ordinary, but they cannot be said to be crazed in fine-mesh.

Series 2, members a, b, and series 3, members a, b, and c, are crazed in fine meshes where the glazes are thick, but only ordinarily crazed where the glazes are thin.

In series 4 again, member a is crazed in fine meshes, while b and c are only moderately crazed, and the remaining members of this series are totally free from crazing.

(3) Nothing can be ascertained from the first four series regarding the relative effect of SiO_2 and B_2O_3 on the coefficient of expansion and contraction of the glazes, for they are nearly alike in this respect, with perhaps slight evidence in favor of B_2O_3 being less effective than SiO_2 in the reduction of the coefficient. This is in keeping with the evidence in these studies.

Series 6. This series is described by itself because it exhibits the most peculiar phenomenon of having little islands of very minute pin-holes widely scattered over the surface of an otherwise normally matured matrix. The beginning of these local boiling spots was noted in the cone 1 burn, where they were slightly raised blisters. At cone 5, however, these blisters have subsided, leaving only roughened pin-holed patches. This phenomenon is unexplainable at present, for it does not resemble in any way the pinholes due to combustion of entrapped carbon.

Other than the defect above noted, all the members of this series were well matured.

Series 7 and 8. Members a, b, c, d, e, of these series are devitrified with a tendency to gloss increasing progressively from a to g, where a very fair gloss is shown.

Summary of Group III at Cone 5.

- (1) All members of the first series of this group may be considered as good glazes, except in case of members a and b, which show fine-mesh crazing to some extent.
- (2) Fine-mesh crazing has decreased rapidly with increase of the oxygen ratio from Group II to Group III.
- (3) B_2O_3 is less effective than SiO_2 in decreasing coefficient of expansion and contraction.
- (4) Devitrification is exhibited only in series 7 and 8, and in these this phenomenon decreases as the Al_2O_3 increases.
- (5) Contrasting the appearance of devitrification in Groups I, II, III it is noted that as the oxygen ratio increases, B_2O_3 becomes more effective in counteracting this phenomenon while Al_2O_3 is if anything, less so.

Fired at Cone 10.

1. All glazes in Group III are decidedly over-burned at Cone 10, with the possible exception of members a, b, c of series 1 and 2, and members b, c, of series 3. Thickly applied as they are in these studies, members of series 1 and 2 are pinholed where thick and in some instances blistered considerably; but near the edges where the glazes have run thin, neither of these defects is noted. The writers hesitate, therefore, in offering an opinion in regard to members of series 1 and 2 at this temperature.

2. Fine-mesh crazing is less pronounced in this group than in the two preceding, and there is also less difference in the extent of fine-mesh crazing between those members which were originally low and those originally high in Al_2O_3 .

3. In this Group at Cone 10, boiling of the mid-members of series 7 and 8 into a light froth has reached its maximum intensity for the entire study. This would seem to indicate that with the oxygen ratio 1:3 we have the greatest fusibility.

Summary of Group III.

(1) Good glazes developed in this group at the various temperatures are as follows:

Series	Cone 010	Cone 05	Cone 1	Cone 5	Cone 10
1	d? e? f?	a b c d e f? g?	a b c d e f g	a? b? c d e f g h	a b c f
2	d? e? f?	a b c d e f? g?	a b c d e f g	a? b? c d e f g h	a b c
3		a b c d e f?	a b c d e f g	a? b? c? d e f g h	a b c
4			a b c d e f	a? b c d e f g h	
5			e? f?	a? b c d e f g h	
6				a? b c d e f g h	
7					
8					

(2) The points of superiority of the glazes of this Group over those of Group I and Group II are as follows:

- a. Longer heat range.
- b. Larger range of composition in the good glazes.

c. Less crazing of the fine-mesh type and more largely of the hair-line type.

d. Less tendency to become dimmed, scummed, or devitrified.

e. Brighter gloss under all heat treatments.

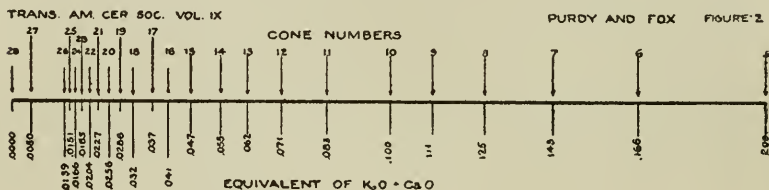
f. Do not eat into the body to a noticeable extent.

(3) At the oxygen ratio 3:1, there is the beginning of an acidity range in which the largest variation in glaze and body composition, as well as the widest range in heat treatment is possible.

(4) It has been noted that the glazes of lower acidity attack the body with the greater avidity. It has also been noted that all the evidence points more directly to the possibility that it is Al_2O_3 rather than SiO_2 which the glaze extracts from the body, for without regard to the acidity of the glaze, fine-mesh crazing ensued only when the original content of Al_2O_3 was low. Yet at this higher acidity, there is but very little eating into the body, and, consequently, fine-mesh crazing is less pronounced.

It is hard to harmonize the two apparently opposing statements last made, unless we grant that silica, although an acid, does not have a solvent power proportional to the amount present in any given case, but that after a certain point has been reached, further additions of silica retards action in a remarkable way. This can be seen in Seger's Al_2O_3 - SiO_2 curve. Near the point of greatest fusibility of mixtures of various silicate materials, there seems to be quite a range in composition without much variation in point of fusion. It is believed that in the case of the fritted glazes under consideration, the point of greatest fusibility is not far from that of which oxygen ratio is 3:1, and that the gradual change in direction of the curve at its lowest point is sufficient to include oxygen ratios ranging from 3 to at least 3.75:1. Addition of acid above that required to establish oxygen ratios within these ranges, whether it is silica or boracic acid, seems to have little effect upon the glass, as it goes into solution very slowly.

This increased range in composition, as the point of maximum fusibility is approached, is graphically seen when the formulæ of Seger comes 5 to 27 inclusive are reduced until Al_2O_3 is equal to unity. By this reduction, the SiO_2 is uniformly reduced to 10, so that if plotted on a straight line, the fractional division in length of which represents the fractional equivalent of RO in the cone formulæ, it will appear that between the point representing cone 6 the distance is equal to that covered by four or five of the highest cones, as is shown in the following figure.

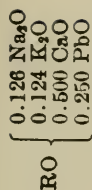


If data were at hand concerning the behavior of mixtures of other mineral ingredients, there is no doubt but that similar phenomena would appear in every case of silicate fusion.

This, then, is the explanation and harmonization of the two seemingly opposite facts that: fine-mesh crazing is due to the extraction of Al_2O_3 , or by increasing the acidity of the glaze.

Group IV.

The table on page 53 shows the compositions of the 64 glazes entering into the group.



Group IV.

$$\text{OR} \left\{ \frac{0 \text{ in acids}}{0 \text{ in bases}} = \frac{3.5}{1} \right.$$

Glaze No.	Al ₂ O ₃ Eqv.	Series No. 1 Ratio 1:0.25		Series No. 2 Ratio 1:0.20		Series No. 3 Ratio 1:0.17		Series No. 4 Ratio 1:0.13		Series No. 5 Ratio 1:0.09		Series No. 6 Ratio 1:0.05		Series No. 7 Ratio 1:0.01		Series No. 8 Ratio 1:0.00	
		SiO ₂	B ₂ O ₃	SiO ₂	B ₂ O ₃	SiO ₂	B ₂ O ₃	SiO ₂	B ₂ O ₃	SiO ₂	B ₂ O ₃	SiO ₂	B ₂ O ₃	SiO ₂	B ₂ O ₃	SiO ₂	B ₂ O ₃
a	0.10	1.6545	0.4136	1.7500	0.3500	1.8128	0.3082	1.9038	0.2475	2.0044	0.1804	2.1163	0.1058	2.2414	0.0224	2.2750
b	0.15	1.8454	0.4614	1.9519	0.3904	2.0219	0.3437	2.1234	0.2760	2.2357	0.2012	2.3605	0.1180	2.5000	0.0250	2.5375
c	0.20	2.0364	0.5091	2.1538	0.4308	2.2311	0.3813	2.3431	0.3046	2.4670	0.2220	2.6046	0.1302	2.7586	0.0276	2.8000
d	0.25	2.2273	0.5568	2.3557	0.4711	2.4402	0.4168	2.5628	0.3332	2.6932	0.2428	2.8488	0.1424	3.0173	0.0302	3.0625
e	0.30	2.4182	0.6045	2.5577	0.5115	2.6494	0.4524	2.7824	0.3617	2.9295	0.2637	3.0930	0.1547	3.2759	0.0327	3.3250
f	0.35	2.6091	0.6523	2.7596	0.5519	2.8586	0.4880	3.0021	0.3903	3.1608	0.2845	3.3372	0.1669	3.5345	0.0353	3.5875
g	0.40	2.8000	0.7000	2.9615	0.5923	3.0677	0.5235	3.2218	0.4188	3.3920	0.3053	3.5814	0.1791	3.7932	0.0379	3.8500
h	0.45	2.9909	0.7477	3.1634	0.6327	3.2769	0.5591	3.4415	0.4474	3.6233	0.3261	3.8255	0.1918	4.0518	0.0405	4.1125
Variation in SiO ₂ per 0.05 eqv. Al ₂ O ₃		0.19091		0.20192		0.20916		0.21997		0.231275		0.24418		0.25863		0.2625	
Variation in B ₂ O ₃ per 0.05 eqv. Al ₂ O ₃		0.04727		0.04038		0.035572		0.028557		0.020816		0.012209		0.002586		

Group IV is so very much like Group III in every way, that it need not be described in detail.

The well matured glazes of this group are as follows:

Series	Cone 010	Cone 05	Cone 1	Cone 5	Cone 10
1	(b to e)?	a b c d e	a b c d e f g	a b c d e f g h?	a b c d e f g
2		a b c d	a b c d e f g	a b c d e f g h?	a b c d e f g
3		a b c	a b c d e f	a b c d e f g h?	b c d e
4			a b c d e f	a b c d e f h?	
5			b c d	a b c d e f g h	
6				a b c d e f g h	
7				c d e	
8					

Group V.

The table on page 55 shows the compositions of the 64 glazes entering into this group.

$$\text{OR} \left\{ \frac{\text{O in acids}}{\text{O in bases}} = \frac{3.75}{1} \right.$$

Group V.

$$\text{RO} \left\{ \begin{array}{l} 0.126 \text{ Na}_2\text{O} \\ 0.124 \text{ K}_2\text{O} \\ 0.500 \text{ CaO} \\ 0.250 \text{ PbO} \end{array} \right.$$

Glaze No.	Al ₂ O ₃ Eqv.	Series No. 1 Ratio 1:0.26		Series No. 2 Ratio 1:0.20		Series No. 3 Ratio 1:0.17		Series No. 4 Ratio 1:0.13		Series No. 5 Ratio 1:0.09		Series No. 6 Ratio 1:0.05		Series No. 7 Ratio 1:0.01		Series No. 8 Ratio 1:0.00	
		SiO ₂	B ₂ O ₃	SiO ₂	B ₂ O ₃	SiO ₂	B ₂ O ₃	SiO ₂	B ₂ O ₃	SiO ₂	B ₂ O ₃	SiO ₂	B ₂ O ₃	SiO ₂	B ₂ O ₃	SiO ₂	B ₂ O ₃
a	0.10	1.7727	0.4432	1.8750	0.3750	1.9422	0.3302	2.0397	0.2652	2.1476	0.1933	2.2674	0.1134	2.4015	0.0240	2.4375
b	0.15	1.9773	0.4943	2.0913	0.4183	2.1663	0.3683	2.2751	0.2958	2.3954	0.2156	2.5291	0.1265	2.6783	0.0267	2.7188
c	0.20	2.1818	0.5454	2.3077	0.4615	2.3904	0.4064	2.5105	0.3264	2.6432	0.2379	2.7907	0.1395	2.9554	0.0295	3.0000
d	0.25	2.3864	0.5966	2.5240	0.5048	2.6145	0.4445	2.7458	0.3570	2.8910	0.2602	3.0523	0.1526	3.2325	0.0323	3.2813
e	0.30	2.5909	0.6476	2.7404	0.5481	2.8386	0.4826	2.9812	0.3876	3.1388	0.2825	3.3140	0.1657	3.5096	0.0351	3.5625
f	0.35	2.7955	0.6987	2.9567	0.5913	3.0627	0.5207	3.2165	0.4182	3.3866	0.3048	3.5768	0.1788	3.7867	0.0378	3.8436
g	0.40	3.0000	0.7499	3.1730	0.6346	3.2868	0.5588	3.4519	0.4487	3.6344	0.3271	3.8372	0.1919	4.0638	0.0406	4.1250
h	0.45	3.2046	0.8011	3.3894	0.6779	3.5109	0.5969	3.6873	0.4793	3.8822	0.3494	4.0989	0.2049	4.3409	0.0434	4.4063
Variation in Silica per 0.05 eqv. Al ₂ O ₃		0.20455		0.21634		0.22410		0.23536		0.24780		0.26168		0.2771		0.28125	
Variation in B ₂ O ₃ per 0.05 eqv. Al ₂ O ₃		0.05113		0.049268		0.038097		0.030597		0.022302		0.0130815		0.002771		

Group V shows once more a narrower range of available composition and limits of heat treatment, as can be judged by the following table which indicates the well matured glazes.

Series	Cone 010	Cone 05	Cone 1	Cone 5	Cone 10
1		a b c d	a b c d e f g	a b c d e f g h	a b c d
2		a b	a b c d e f	a b c d e f g h	a b c d
3		a b	a b c d e f	a b c d e f g h	a b
4		a	a b c d e f	a b c d e f g h	
5			a b c	a b c d e f	
6			a	b c d	
7					
8					

In Group III, at Cone 10, there was exhibited some tendency of the glazes low in Al_2O_3 to attack the body, while in Group IV but a slight trace of such action was noted. In Group V, however, eating into the body and a consequent development of fine-mesh crazing is again seen.

A decided opalescence is shown in member a of series 1, 2, and 3 at cone 10. This is the first occurrence of this peculiar super-saturation effect.

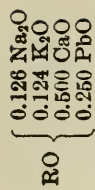
The slow rate at which glass formation proceeds when high in Al_2O_3 , is very strikingly shown in the case of members e, f, g, h of series 1 and 2 of Groups IV to VII. At 010, these glazes have passed thru the first boiling stage, and are fairly smooth glasses containing some undissolved material. It requires a heat treatment extending over a range of 10 cones or more to effect complete solution. In some cases, notably in the h members, the glazes will pass into the second boiling stage before complete solution of all the incorporated material has been attained. It is noted also that this peculiarity was more in evidence at the lower oxygen ratios, less so in Group III, which has an oxygen ratio of 1:3, and then again becomes progressively more pronounced as the oxygen ratio increases from 1:3 to 1:4.5.

In the lower oxygen ratios, glazes having a medium Al_2O_3 content had the longest heat and composition range. At oxygen ratio of 1:3, there was less discrimination in this regard, while at higher oxygen ratios, it is the glazes that have the lowest content of Al_2O_3 that show the longest heat and composition range.

Explanation of this reversal in effect of Al_2O_3 at different oxygen ratios will be given after describing Groups VI and VII.

Group VI.

The table on page 58 shows the compositions of the sixty-four glazes composing this group.



Group VI.

$$\text{OR} \left\{ \begin{array}{l} \text{O in acids} \\ \text{O in bases} \end{array} \right. = \frac{4}{1}$$

Glaze No.	Al ₂ O ₃ Eqv.	Series No. 1 Ratio 1:0.25		Series No. 2 Ratio 1:0.20		Series No. 3 Ratio 1:0.17		Series No. 4 Ratio 1:0.13		Series No. 5 Ratio 1:0.09		Series No. 6 Ratio 1:0.05		Series No. 7 Ratio 1:0.01		Series No. 8 Ratio 1:0.00	
		SiO ₂	B ₂ O ₃	SiO ₂	B ₂ O ₃	SiO ₂	B ₂ O ₃	SiO ₂	B ₂ O ₃	SiO ₂	B ₂ O ₃	SiO ₂	B ₂ O ₃	SiO ₂	B ₂ O ₃	SiO ₂	B ₂ O ₃
a	0.10	1.8909	0.4727	2.0000	0.4000	2.0717	0.3522	2.1757	0.2828	2.2908	0.2062	2.4186	0.1209	2.5616	0.0256	2.60
b	0.15	2.1091	0.5273	2.2308	0.4462	2.3108	0.3928	2.4268	0.3155	2.5551	0.2300	2.6977	0.1349	2.8571	0.0286	2.90
c	0.20	2.3273	0.5818	2.4615	0.4923	2.5498	0.4355	2.6778	0.3481	2.8194	0.2537	2.9767	0.1488	3.1527	0.0315	3.20
d	0.25	2.5455	0.6364	2.6923	0.5385	2.7888	0.4741	2.9289	0.3808	3.0837	0.2775	3.2558	0.1628	3.4483	0.0345	3.50
e	0.30	2.7636	0.6909	2.9231	0.5846	3.0279	0.5147	3.1799	0.4134	3.3480	0.3013	3.5349	0.1767	3.7439	0.0374	3.80
f	0.35	2.9818	0.7454	3.1539	0.6308	3.2669	0.5553	3.4309	0.4460	3.6123	0.3251	3.8140	0.1907	4.0394	0.0404	4.10
g	0.40	3.2000	0.8000	3.3846	0.6769	3.5080	0.5960	3.6820	0.4787	3.8766	0.3489	4.0930	0.2046	4.3850	0.0434	4.40
h	0.45	3.4182	0.8545	3.6154	0.7231	3.7450	0.6366	3.9330	0.5113	4.1409	0.3727	4.3721	0.2186	4.6306	0.0463	4.70
Variation in SiO ₂ per 0.05 eqv. of Al ₂ O ₃		0.21818		0.23077		0.23904		0.25104		0.26491		0.27907		0.29557		0.30	
Variation in B ₂ O ₃ per 0.05 eqv. Al ₂ O ₃		0.05454		0.04615		0.040637		0.032635		0.02379		0.01395		0.002956		

Fired at Cone 010.

Group VI at this cone is wholly immature. No efflorescence.

Members of Series 8 are perfectly flat and are porcelain-like in character.

Fired at Cone 05.

Series 1, 2, 3. The following series were well matured and completely in solution.

Series 1 a, b, c, d.

Series 2 a, b, c, d.

Series 3 a, b, c, d.

While the above members had reached good maturity, members g and h of the same series were just subsiding from the first boiling stage.

Series 4, 5. The members of these series were all immature glasses more or less full of undissolved materials. Members a and b are almost clear.

Series 6, 7, 8, were porcelanic in character, decreasing in glossiness with decrease in proportion of B_2O_3 to SiO_2 .

Fired at Cone 1.

Series 1 and 2. Members a to g inclusive are good glazes. h has some undissolved material. a and b are the only members of this series that are crazed.

Series 3 and 4. Members a to e of this series are well developed. g and h have not settled down to a flat surface.

Series 5 and 6. Members a, b, c, d of this series are promising. The remaining members have not reached quiet fusion as yet.

Series 7. Member a is fairly good glaze, while the remaining series are porcelanic in character.

Series 8 are porcelanic in appearance, resembling an average white Bristol glaze.

Fired at Cone 5.

Series 1 to 5 inclusive. Every member of these series except members a of series 4 and 5, are good glazes. a of series 4 and 5 are crazed in extremely fine meshes.

Series 6 and 7. This is the only group which seems to have been smoked at Cone 5, and as a consequence there is in these series the phenomena, before noted, of patches of pin-holes in an otherwise smooth, well-matured matrix. Members c, d, e, and f, present such an appearance in series 6 and 7.

Series 8. Member d of Series 8, Group VI, is the first instance of any of the glazes of this series maturing, except in case of d Series 8, Group 1.

Fired at Cone 10.

The only good glazes in this group at Cone 10 were Series 5 and 6, members g and h. All other glazes were over-burned.

Summary of Group VI. The good glazes are as follows:

Series	Cone 010	Cone 05	Cone 1	Cone 5	Cone 10
1		a b c d	a to g	a to h	
2		a b c d	a to g	a to h	
3		a b c d	a b c d e	a to h	
4		a b	a b c d e	b to h	
5		a b	a b c d	b to h	g h
6			a b c d	c d e	g h
7			a	c d e	
8				d	

(2) Opalescence phenomena are shown in member "a" of Series 1, 2, 3, 4, at Cone 5 and 10.

Group VII.

The table on page 61 gives the composition of the 64 glazes composing this group.

$$\text{OR} \left\{ \frac{\text{O in acids}}{\text{O in bases}} = \frac{4.5}{1} \right.$$

Group VII.

$$\text{RO} \left\{ \begin{array}{l} 0.128 \text{ Na}_2\text{O} \\ 0.124 \text{ K}_2\text{O} \\ 0.500 \text{ CaO} \\ 0.250 \text{ PbO} \end{array} \right.$$

Glaze No.	Al ₂ O ₃ Eqv.	Series No. 1 Ratio 1:0.25		Series No. 2 Ratio 1:0.20		Series No. 3 Ratio 1:0.17		Series No. 4 Ratio 1:0.13		Series No. 5 Ratio 1:0.09		Series No. 6 Ratio 1:0.05		Series No. 7 Ratio 1:0.01		Series No. 8 Ratio 1:0.00	
		SiO ₂	B ₂ O ₃	SiO ₂	B ₂ O ₃	SiO ₂	B ₂ O ₃	SiO ₂	B ₂ O ₃	SiO ₂	B ₂ O ₃	SiO ₂	B ₂ O ₃	SiO ₂	B ₂ O ₃	SiO ₂	B ₂ O ₃
a	0.10	2.1273	0.5318	2.2500	0.4500	2.3307	0.3992	2.4477	0.3182	2.5771	0.2319	2.7209	0.1360	2.8818	0.0288	2.9250
b	0.15	2.3727	0.5932	2.5096	0.5019	2.5996	0.4419	2.7301	0.3549	2.8745	0.2588	3.0349	0.1517	3.2443	0.3244	3.2625
c	0.20	2.6182	0.6546	2.7692	0.5538	2.8885	0.4876	2.9126	0.3916	3.1718	0.2855	3.3488	0.1674	3.5468	0.0355	3.6000
d	0.25	2.8636	0.7159	3.0288	0.6058	3.1375	0.5334	3.1950	0.4283	3.4692	0.3122	3.6683	0.1831	3.8793	0.0388	3.9375
e	0.30	3.1091	0.7773	3.2884	0.6577	3.4064	0.5791	3.4773	0.4650	3.7665	0.3390	3.9767	0.1988	4.2118	0.0421	4.2750
f	0.35	3.3545	0.8387	3.5481	0.7096	3.6753	0.6248	3.7597	0.5018	4.0639	0.3657	4.2907	0.2145	4.5443	0.0454	4.6125
g	0.40	3.6000	0.9000	3.8077	0.7615	3.9442	0.6705	4.0422	0.5385	4.3613	0.3925	4.6046	0.2302	4.8768	0.0488	4.9500
h	0.45	3.8454	0.9614	4.0673	0.8134	4.2132	0.7162	4.4246	0.5752	4.6586	0.4193	4.9186	0.2459	5.2093	0.0521	5.2875
Variation in SiO ₂ per 0.05 eqv. of Al ₂ O ₃		0.24545		0.25961		0.26863		0.28243		0.29736		0.31395		0.33251		0.3375	
Variation in B ₂ O ₃ per 0.05 eqv. of Al ₂ O ₃		0.06137		0.05192		0.045718		0.03671		0.02676		0.01569		0.003325		

Fired at Cone 010.

Group VII at Cone 010 was so badly carbonized that little can be said in regard to it except that members a and b of the first three series were approaching the stage of quiet fusion.

Fired at Cone 05.

Series 1, 2, 3. Each of these series presents a well matured finish at the low Al_2O_3 end, and not complete subsidence from the first boiling stage at the high Al_2O_3 end.

In the first four members of Series 1, and the first two of Series 2 and 3, there is a peculiar milky appearance.

Series 4 to 8. These series show successive gradation from glass to a porcelanic mass.

The members of Series 8, and especially those low in Al_2O_3 , resemble very much the opalite tile bodies.

Fired at Cone 1.

Series 1, 2, 3. All members of these series have reached the first quiet fusion stage.

The following glazes appear to have reached their full maturity:

Series 1 a, b, c, d, e f.

Series 2 a, b, c, d, e, f.

Series 3 a, b, c, d.

In members b, c, d, e of Series 1, and e, d, of Series 2 and 3, the milky cloudiness noted at Cone 05 has developed into opalescent crystals. This phenomenon reaches its maximum development in member c of Series 1.

Series 4, 5. These series have not progressed much beyond the first boiling stage at the high Al_2O_3 end, but are well matured at the low Al_2O_3 end.

The following are the members developed at Cone 1:

Series 4 a, b, c.

Series 5 a, b, c.

Series 6, 7, 8. Are all immature.

Fired at Cone 5.

The following glazes of this group were well matured at Cone 5:

Series 1 a, b, c, d, e, f, g, h.

Series 2 a, b, c, d, e, f, g, h.

Series 3 a, b, c, d, e, f, g, h.

Series 4 a, b, c, d.

Series 5 a, b.

Series 6 a.

Opalescence was developed in the following glazes:

Series 1 a, b, c, d, e.

Series 2 a, b, c.

Series 3 a, b.

Series 4 a.

The opalescent effects in c, Series 1, are the most perfect the writers have ever seen.

Remaining members of the group are either over-fired or immature.

Fired at Cone 10.

Summary: Since there are only five distinctive features brought out in the Group at Cone 10, detailed description of the separate series will not be given.

(1) Members a of Series 1 and 2 were the only glazes of this group that were developed at Cone 10. The others were either immature or over-burned.

(2) Opalescent effects at this temperature have passed from the crystalline to flowed opaque streaks.

(3) Quick passage from an immature to an over-burned condition of these glazes high in Al_2O_3 is as pronounced in this group as in Group V and VI.

(4) This narrowness in maturing range is more pronounced in the series low in B_2O_3 .

(5) Attack on the body by the glazes is not noticeable even at Cone 10.

SUMMARY OF RESULTS.

Heat Range.

It was thought that a study of the heat range of the several glazes could best be made by taking them up in eight charts, on the basis of an equal Al_2O_3 content. Accordingly curves have been drawn in which the SiO_2 - B_2O_3 ratio is plotted on the abscissa, and the oxygen ratio on the ordinate. The curves thus plotted show the thermal boundaries within which the glazes will mature. In drawing these curves accidentally good or bad glazes, lying wholly outside of their proper areas were ignored. The thermal limits shown are the extremes. It is obvious that it would not be advisable to reach these extremes in practice.

Figure 3.

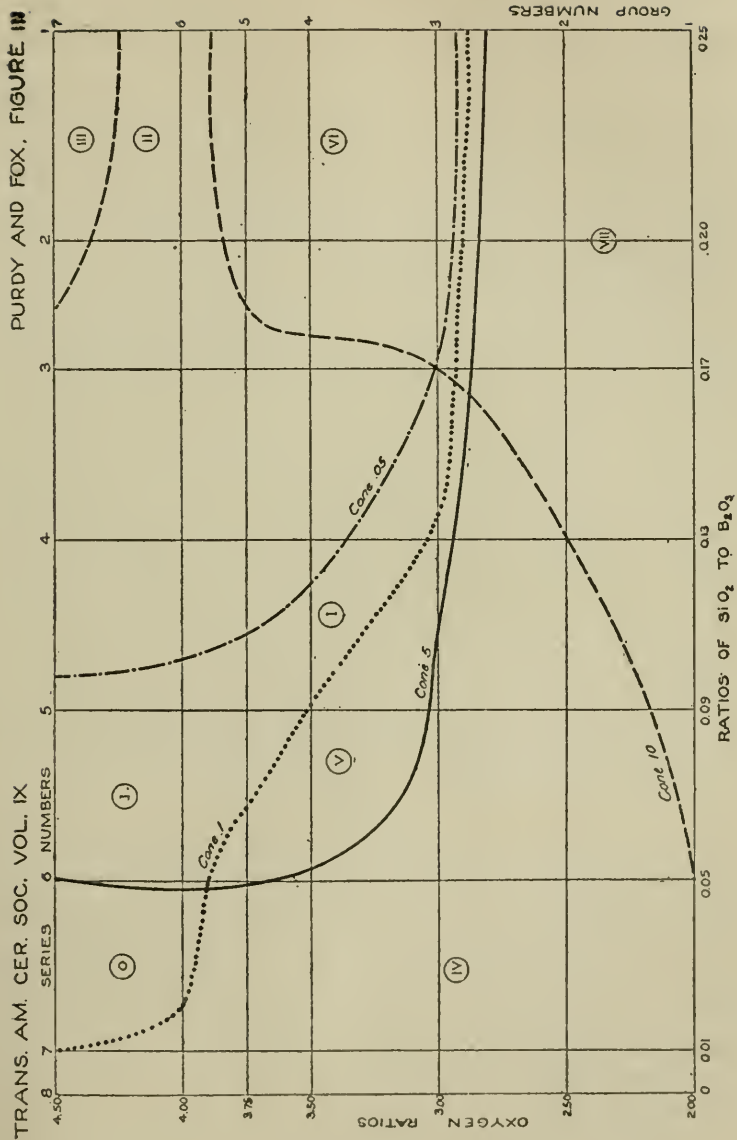
Figure 3 shows the thermal boundary limits of maturity for the a glazes, which have an Al_2O_3 content of 0.10 equivalents.

The areas included within these lines have been designated by Roman numerals, in order to make their identification in the text easier.

The glazes to the right of the thermal lines are well matured, within the limits shown.

Glazes plotted in the area marked O do not reach their full maturity before Cone 1 is attained, and are on the verge of being over-burned at Cone 5.

Glazes plotted in the upper portion of area I have a



heat range from Cone 05 to 5, while those in the lower portion of this area have a range only from Cone 05 to Cone 1.

Glazes plotted in area II have a heat range from Cone 05 to 5. As the B_2O_3 increases in proportion to SiO_2 , the glazes of this area have their heat range increased, until those highest in B_2O_3 can withstand Cone 10. The glazes having a heat range that includes Cones 05 and 10 are those plotted in areas III and VI.

Glazes plotted in area IV are either immature or over-burned. Those having an oxygen ratio of 4.0 to 4.5 are over-burned at Cone 5, and the others not until Cone 10 has been reached.

Glazes in area V have a heat range from Cone 1 to Cone 5.

Glazes in area VII practically have no heat range. Below Cone 10 they are so thoroughly crazed in fine meshes that they must be ruled out as glazes, although where B_2O_3 is high, they may be good glasses. At Cone 10 they are well developed glazes, being crazed only in hair lines.

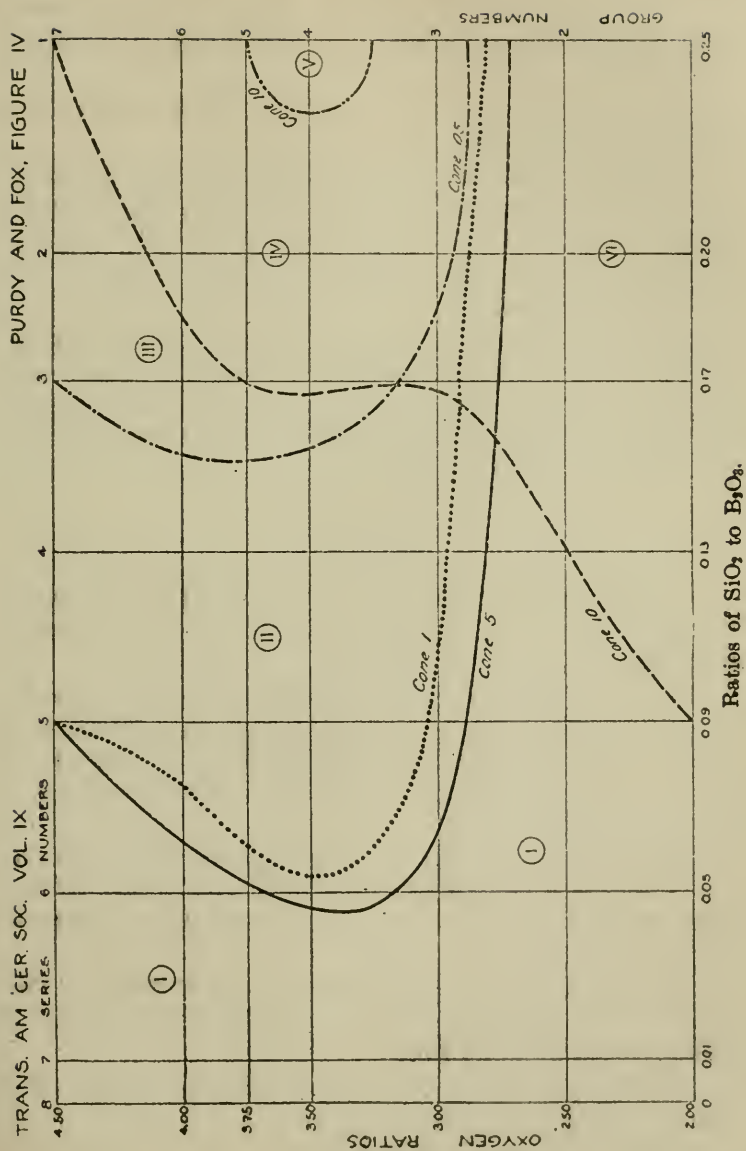
The glazes containing only 0.10 equivalents Al_2O_3 have the longest heat range with the O. R. range 3.0 to 4.0, and SiO_2 - B_2O_3 ratio range of 0.25 to 0.17.

Figure 4.

Glazes plotted in the upper portion of area I are over-burned at Cone 5, while those plotted in the lower portion or area I and near to the Cone 10 thermal curve are not over-burned until Cone 10 is reached, while those lying further away from the Cone 10 curve remain immature until Cone 10 has been reached.

Glazes plotted in area II have a heat range from Cone 05 to Cone 5.

Glazes plotted in area III close to the Cone 05 thermal line are good at Cone 05 and, as the content of B_2O_3



increases at the expense of SiO_2 , the heat range increases until those plotted in area IV have a range from Cone 05 to Cone 10.

The one glaze plotted in area V has a heat range from Cone 010 to Cone 10.

Glazes in area VI, like those plotted in a corresponding area in Figure 3, are in some cases good glasses at heats lower than Cone 10, but, owing to their extremely fine mesh crazing, they cannot be classed as glazes until Cone 10 is reached.

Aside from glaze b of Series 1, Group IV, the glazes having the longest heat range, with Al_2O_3 content equal to 0.15 equivalent, are found in Series 1, 2 and 3 of Group III to VI, inclusive. These glazes have a heat range from Cone 05 to Cone 10, inclusive.

Figure 5.

Glazes plotted in area I are immature until Cone 10 is reached, and then they pass directly into an over-burned condition.

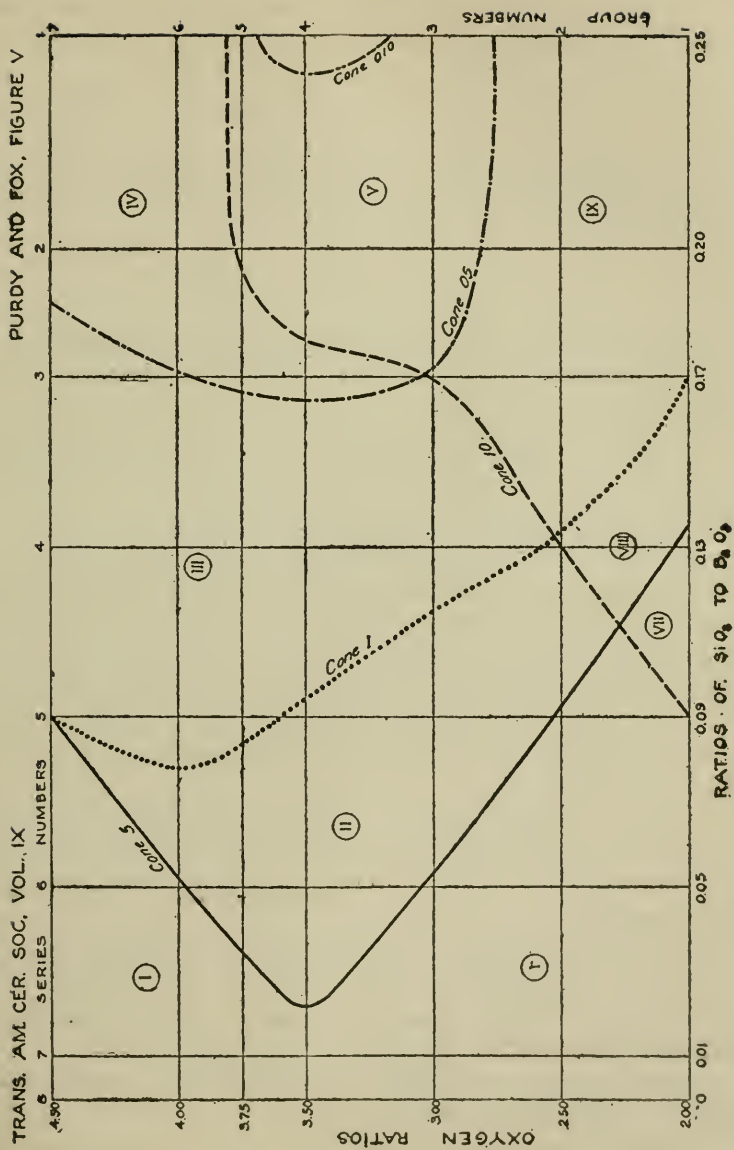
Glazes plotted in the upper portion of area III have a heat range from Cone 1 to Cone 5; those contiguous to the Cone 1 thermal curve are barely matured at Cone 1, and those nearer the thermal curve of Cone 5 are decidedly immature at Cone 1.

Glazes plotted in the upper portion of area III have a heat range that extends from Cone 05 to 5, while the heat range of those in the lower portion of area III extends close to Cone 10.

Glazes in area IV have a heat range from Cone 05 to Cone 5. Those plotted near the Cone 05 thermal curve are just matured at Cone 05.

Glazes plotted in area VII have a heat range from Cone 5 to Cone 10, being not quite matured at Cone 5.

Glazes plotted in area VIII have a heat range from Cone 1 to Cone 10, being barely matured at Cone 1.



Glazes plotted in area IX have a heat range from Cone 1 to Cone 10, being fully matured at Cone 1.

Glazes plotted in area V have a heat range from Cone 05 to Cone 10, being fully matured at Cone 05.

The maximum heat range then of glazes containing 0.2 equivalent of Al_2O_3 , is to be found in Series 1, 2 and 3 of Groups III to V, inclusive.

Figure 6.

Glazes plotted in area I are over burned at Cone 5.

Glazes plotted in area II are immature at Cone 5, but over-burned at Cone 10.

Glazes plotted in area III have a heat range from Cone 1 to Cone 5. Those of the lower portion are harder than those of the upper portion of this area.

Glazes plotted in area IV have a variable heat range, those having an oxygen ratio of 4.5 showing a range from Cone 1 to Cone 5; those having an oxygen ratio of 3.5 to 4, inclusive, showing a range from Cone 1 to Cone 10, when B_2O_3 is high, while those having an oxygen ratio of 2.5 to 3.5 show a range from Cone 05 to Cone 5. No explanation of this variableness in heat range of the glazes of the area can be offered.

Glazes plotted in area V have a heat range of Cone 1 to 10.

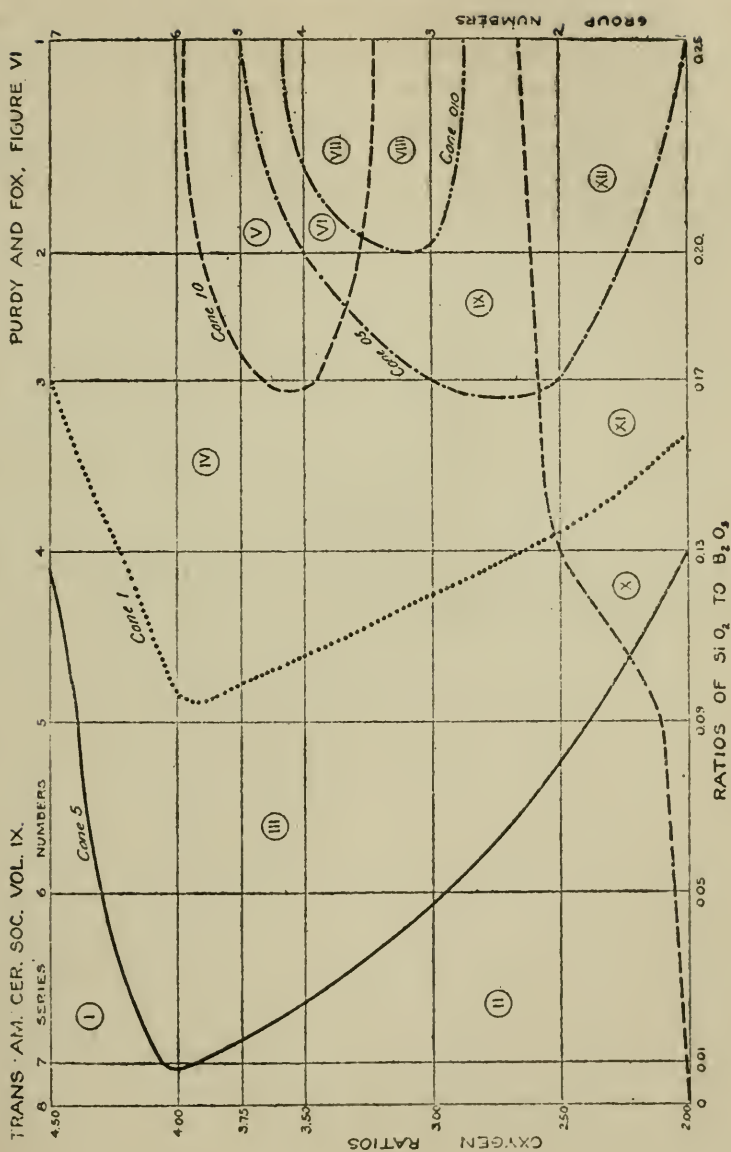
Glazes plotted in area VI have a heat range from Cone 05 to Cone 10.

Glazes plotted in area VII have a heat range from Cone 010 to Cone 10.

Glazes plotted in area VIII have a heat range from Cone 010 to Cone 5.

Glazes plotted in area IX have a heat range that averages from Cone 05 to Cone 5.

Glazes plotted in area X have a heat range that extends only from 1 to 10.



Glazes plotted in areas XI and XII have a heat range from 05 to 10, those in area XI being immature and those in area XII being fully matured at Cone 05.

The glazes having the longest heat range are those plotted in areas V, VI, VII, VIII, IX and XII, or those having an oxygen ratio of from 2.5 to 4.0, inclusive, and a $\text{SiO}_2\text{-B}_2\text{O}_3$ ratio of 0.17 to 0.25.

Figure 7.

The description of Figure 6 applies to Figure 7, except for minor details.

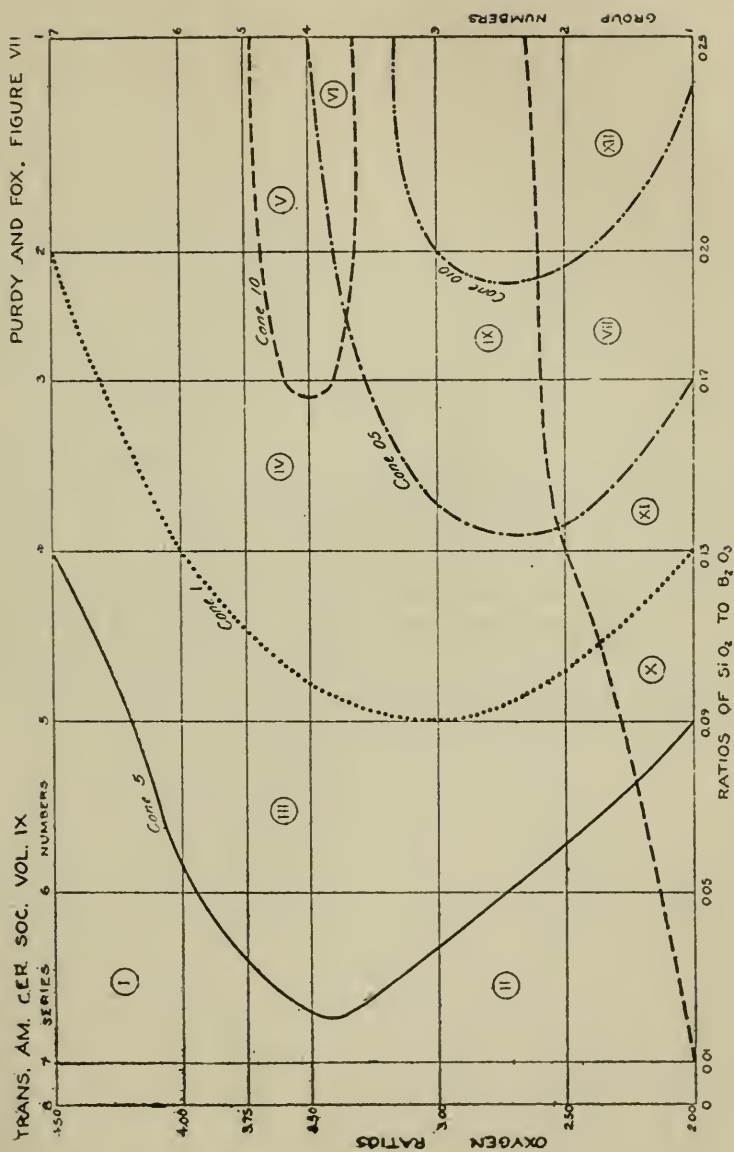


Figure 8.

Glazes of all areas except I, VII and VIII have heat ranges, the maximum points of which are Cone 5 in the case of II and III, and Cone 10 in the case of IV, V and VI, and the minimum points of which lie in the curve bounding them on the right, except in case of III.

The longest heat range shown in the case of glazes having 0.35 Eqv. content of Al_2O_3 , is found at the oxygen ratios of 2.0 to 3.50, inclusive, and a $\text{SiO}_2\text{-B}_2\text{O}_3$ ratio of from 0.25 to 0.17.

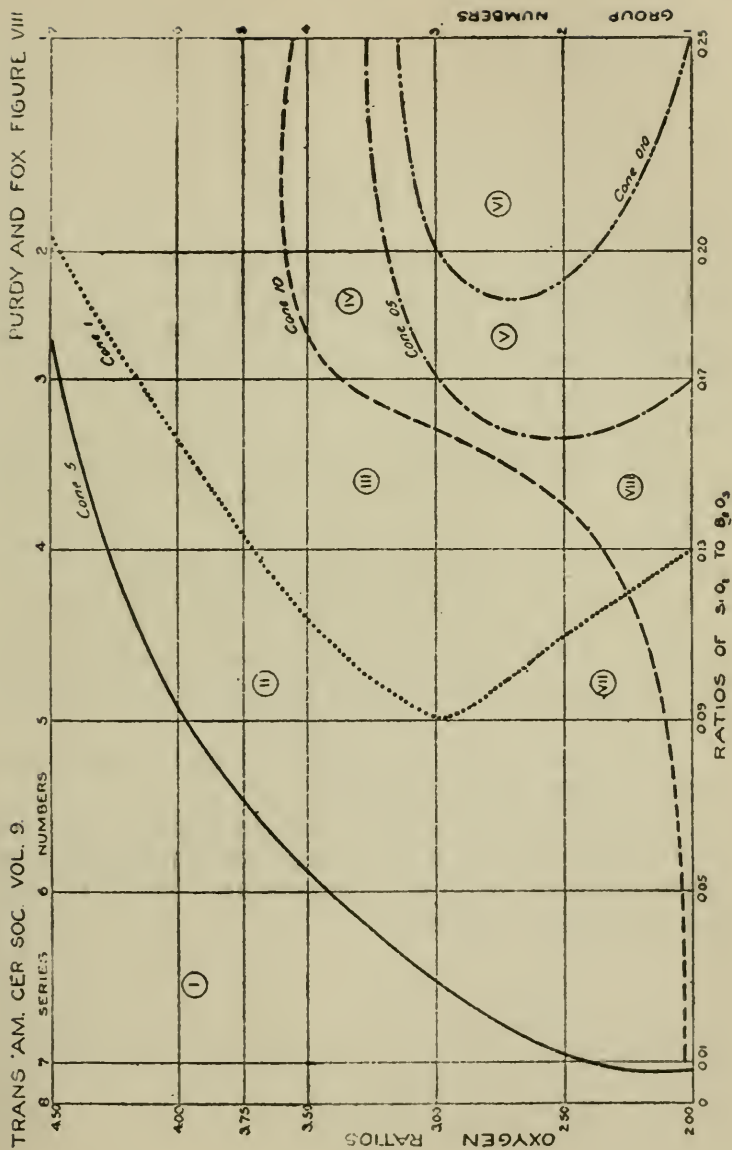


Figure 9.

Glazes plotted in area I were immature even at Cone 10, except when the oxygen ratio is low.

Glazes plotted in area II have a heat range from Cone 1 to Cone 5.

Glazes plotted in area III have a heat range from Cone 1 to Cone 10.

Glazes plotted in area IV have a heat range from Cone 05 to 5 or more, being somewhat immature at Cone 05.

Glazes plotted in area V have a heat range from Cone 05 to nearly Cone 10, being fully matured at Cone 05.

Glazes plotted in area VI have a heat range that extends from a little above Cone 05 to Cone 10, while those of area VII have a heat range that extends from Cone 05 to Cone 10.

The glazes plotted in area VIII have a heat range from Cone 010 to 10, inclusive.

The glazes having an Al_2O_3 content of 0.40 equivalents and showing the longest heat range, are found within the oxygen ratios of 2.0 to 3.5, inclusive and $\text{SiO}_2\text{-B}_2\text{O}_3$ ratio from 0.25 to 0.20, inclusive.

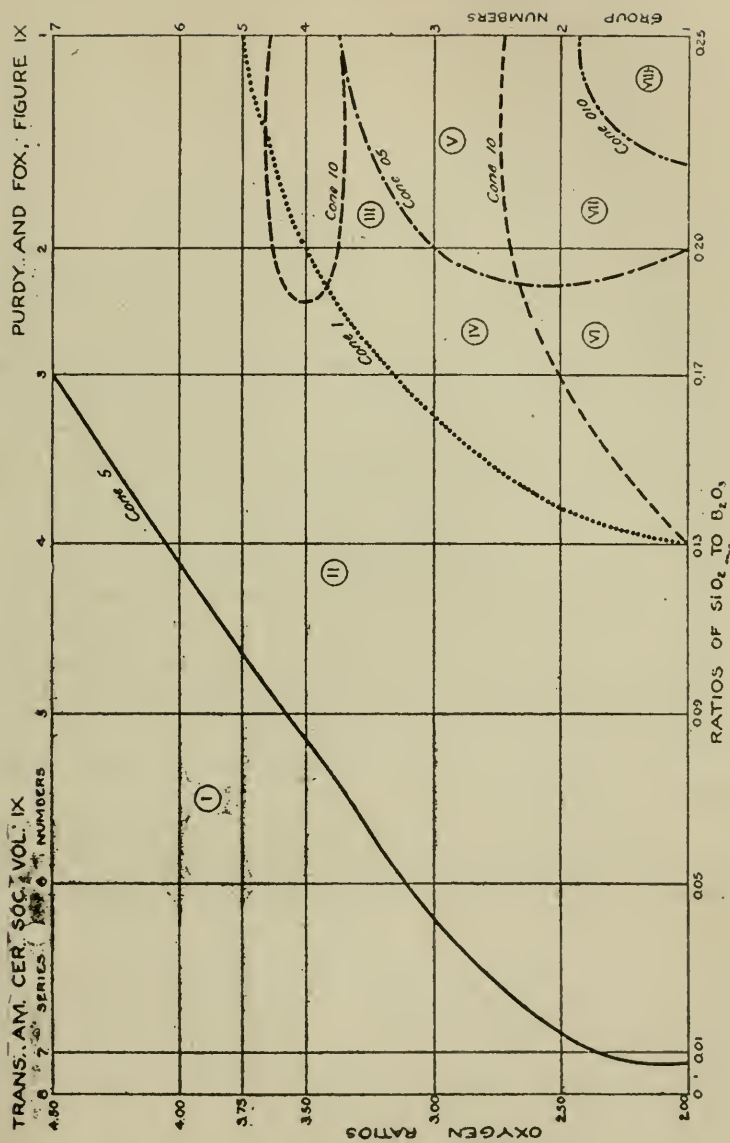


Figure 10.

Glazes plotted in area I were not matured at Cone 5 or 10.

Glazes plotted in area II were good at Cone 5. Those to the extreme left were barely matured and had a short heat range, while those to the extreme right were fully matured and had a heat range from Cone 5 almost to Cone 10 in all cases and in some cases from Cone 1 to 10.

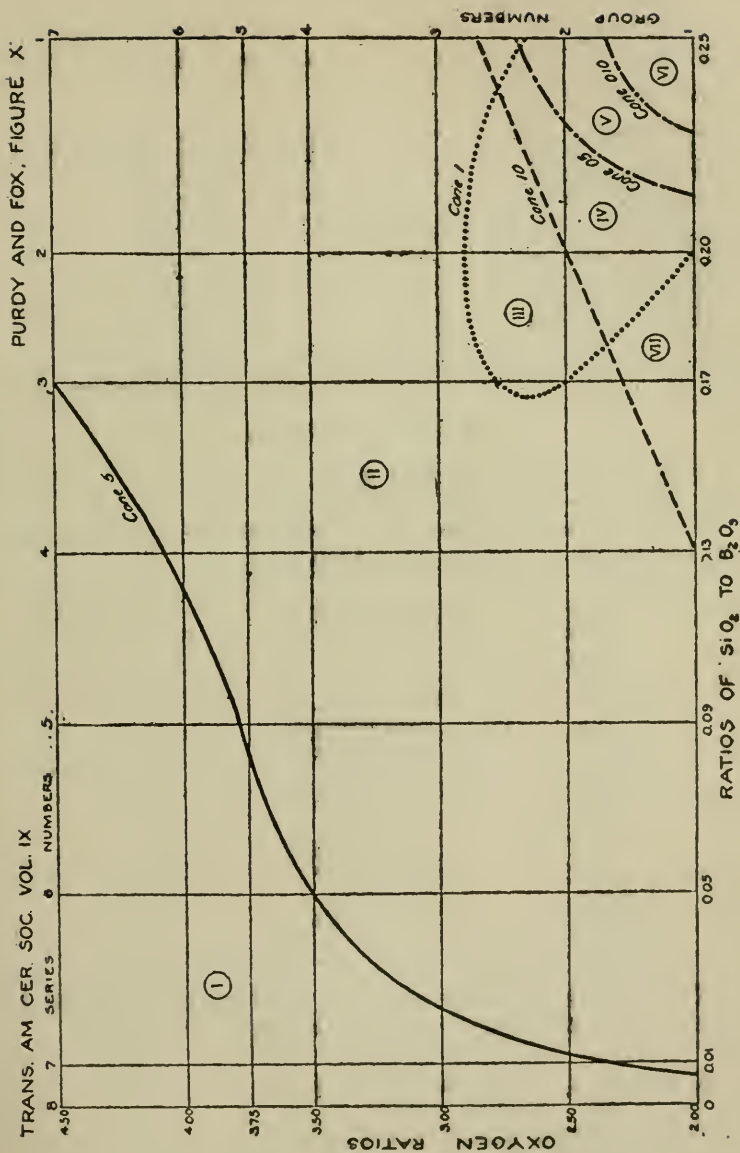
Glazes plotted in area III have a heat range from Cone 1 to almost 10, being over-fired at Cone 10.

Glazes plotted in area IV have a heat range that varies from Cone 05 to Cone 10 and those in area V from Cone 010 to Cone 10, being rather immature at Cone 010.

Glazes plotted in area VI were good from Cone 010 to Cone 10, inclusive.

Glazes plotted in area VII have a heat range from Cone 1 to Cone 10.

The greatest heat range shown by glazes containing $0.45 \text{ Al}_2\text{O}_3$ is found within the oxygen ratio of 2.0 to 3.0, and a $\text{SiO}_2\text{-B}_2\text{O}_3$ ratio that averaged about as 1:2.0.



Summary on Heat Range: (1) In the following table is shown the limits of composition, within which the longest heat range was obtained.

Eqv. Al_2O_3 Content	Oxygen Ratio	$SiO_2 - B_2O_3$ Ratio	Average Maximum Heat Range in Cones
0.10	3.0-4.0	0.25-0.17	05-10
0.15	3.0-4.0	0.25-0.17	05-10
0.20	3.0-3.75	0.25-0.17	05-10
0.25	2.5-3.75	0.25-0.17	05-10
0.30	2.0-3.50	0.25-0.17	010-10
0.35	2.0-3.50	0.25-0.17	010-10
0.40	2.0-3.50	0.25-0.20	05-10
0.45	2.0-3.50	0.25-0.20	05-10

Composition Range.

Member a. $Al_2O_3=0.10$ Eqv.

The following glazes are well matured and crazed only in hair lines at the cones indicated:

Groups	Series	Heat Range in Cones	Free From Crazing
I	None		
II	None		
III	{ 1, 2, 3, 4, 5,	05-5 1	
IV	{ 1, 2 3 4	05-10 inclusive 05-5 inclusive 5	
V	{ 1, 2, 3, 4, 5, 6,	05-5 inclusive 1	
VI	{ 1, 2, 3, 4, 5, 6, 7,	05-5 inclusive 05-5 inclusive 1	
VII	{ 1, 2, 3, 4, 5, 6, 7,	05-5 inclusive 1	

The others are matured at heat ranges shown in Figure 3, but are crazed in fine meshes.

Member b. $Al_2O_3=0.15$ Eqv.

The following glazes are well matured, and crazed, if at all, only in hair lines at cones indicated. Those free from crazing are indicated in the fourth column.

Groups	Series	Heat Range in Cones	Free From Crazing
I	None		
II	None		
III	{ 1, 2, 3, 4, 5, 6,	05-5 1	
IV	{ 1, 2, 3, 4	05-5 inclusive 1	at cone 1 at cone 1
V	{ 1, 2, 3, 4	05-5 inclusive 1	at cone 1 at cone 1
VI	{ 1, 2, 3, 4, 5, 6,	05-5 inclusive 1-5 inclusive	Series 1 at cone 5 Series 2 3 4 5 6 at Cone 1
VII	{ 1, 2, 3, 4, 5,	05-5 inclusive 1	Series 1 at Cone 05-5 Series 2, 3, 4, 5, at Cone 1

The remainder are matured at heat ranges shown in Figure 4, but are crazed in fine meshes.

Member c. $Al_2O_3=0.20$ *Eqv.*

The following glazes are well matured and crazed, if at all, only in hair lines at cones indicated. Those free from crazing are indicated in the fourth column.

Group	Series	Heat Range in Cones	Free From Crazing
I			
II	2, 3	1	
III	{ 1, 2, 3, 4, 5, 6,	05-5 1	
IV	{ 1, 2, 3, 4,	05-5 inclusive 1-5 inclusive	at cone 1 at cone 1
V	{ 1, 2, 3, 4, 5,	05-5 inclusive 1-5	at cone 1-5 inclusive at cone 1-5 inclusive
VI	{ 1, 2, 3, 4, 5,	05-5 inclusive 1-5 inclusive	cone 1-5 inclusive cone 1
VI	{ 1, 2, 3, 4, 5,	05-5 inclusive 1-5 inclusive	cone 1-5 inclusive cone 1

The remainder are matured at heat ranges shown in Figure 5, but are crazed in fine meshes.

Member d. $Al_2O_3=0.25$ *Eqv.*

The following glazes are well matured and crazed, if at all, only in hair lines at cones indicated. Those free from crazing are indicated in the fourth column.

Group	Series	Heat Range in Cones	Free From Crazing
I			
II	{ 1 2, 3, 4, 5, 6,	010-1 inclusive 05-5 inclusive 5	Series 4 at Cone 5
III	{ 1, 2, 3, 4, 5, 6	05-5 inclusive 1-5 inclusive 5	Series 3, 4 at cones 1-5
IV	{ 1, 2, 3, 4,	05-5 inclusive 1-5 inclusive 5	1, 2, 3, at cone 1 1, 2, 3, at cones 1-5
V	{ 1, 2, 3,	05-010 inclusive 1-5 inclusive	1, 2, 3, at cones 1-5
VI	{ 1, 2, 3, 4, 5, 6, 7,	1-5 5	2, 3, 4, at cones 1-5 5, 6, 7, at cone 5
VII	{ 1, 2, 3, 4,	1-5 5	1, 2, 3, at cones 1-5 4 at cone 5

The remaining glazes are matured at heat ranges shown in Figure 6, but are crazed in fine meshes.

Member c. $Al_2O_3=0.30$ Eqv.

Group	Series	Heat Range in Cones	Free from From Crazing
I	{ 1, 2, 3, 4	05-5 inclusive 1-5 inclusive	None
II	{ 1 2, 3, 4, 5, 6,	05-5 inclusive 1-5 inclusive 5	4, 5, 6, at cone 5
III	{ 1, 2, 3, 4, 5, 6,	05-5 inclusive 1-5 inclusive 5	1,2,3,4, at cones 1-5
IV	{ 1, 2, 3, 4 5-6	1-10 inclusive 1-5 5	1, 2, 3, at cones 1-10 4 at cones 1-5 5, 6, at cone 5
V	{ 1, 2, 3, 4, 5, 6,	1-5 inclusive 5	1, 2, 3,4, at cones 1-5 5, 6, at cone 5
VI	{ 1, 2, 3, 4, 5	1-5 inclusive 5	1, 2, 3,4, at cones 1-5
VII	{ 1, 2, 3, 4,	1-5 inclusive 5	1, 2, at cones 1-5 3, 4, at cone 5

The remaining glazes are matured at heat ranges shown in Figure 7, but are crazed in fine meshes.

as to produce a cloudy or milky appearance. When over-fired, the effect is similar to the curdiness produced in a glaze by addition of raw tin oxide. When fired to the best maturity of the glaze, the opalescent effects produced by supersaturation with SiO_2 are distinctly crystalline.

(5) While the writers have advanced the opinion that this opalescent effect is produced by supersaturation and separating out of SiO_2 , they can offer no evidence contradictory to the hypothesis that the material thus separated out is a borate. High content of B_2O_3 is required, and the opalescence here described not only does not appear unless B_2O_3 is proportionately high, but it increases in intensity and is produced in wider and wider variation as the B_2O_3 increases in proportion to SiO_2 . The writers have based their opinion that this phenomenon is due to the supersaturation of the glaze by SiO_2 , on the chemical composition of milky opals as they occur in nature.

ATTACK ON THE BODY.

The supposition has been advanced that Al_2O_3 is the principal constituent taken from the body by the glaze. The facts that support this assumption are as follows:

(1) The glazes lowest in Al_2O_3 (0.10—0.20 Eqv.) show this phenomenon to the greatest extent.

(2) The glazes lowest in Al_2O_3 show the fine-mesh crazing which results from incorporating constituents from the body into the glaze layer that is contiguous to the body, irrespective of oxygen ratio. It is a fact, however, that fine-mesh crazing decreases as the oxygen ratio increases, but this is attributed to the approximate saturation of the matrix with acid, as is evidenced in the appearance of opalescence as early as Group VI.

(3) Glazes having a low oxygen ratio, and low Al_2O_3 content, decrease in fine-mesh crazing as the intensity of heat increases.

(4) Glazes that craze in fine meshes when thick are crazed only in hair lines when thin.

(5) Increase of originally added Al_2O_3 decreases fine-mesh crazing under less intense temperatures, but increases it as the temperature becomes more intense.

(6) Fine-mesh crazing is certainly due to lack of homogeneity in the composition of the upper and lower surface of the glaze layer, and this lack of homogeneity is more pronounced, the more viscous the glaze is rendered by the incorporated constituent.

(7) Fine-mesh crazing developed at temperatures below Cone 5, can be counteracted by increasing the Al_2O_3 content of the glaze. If it is developed at higher heats, it can be counteracted by decreasing the Al_2O_3 content, especially when the oxygen ratio is low.

PIN-HOLING.

Pin-holing and blistering has been proven in these studies to be primarily due to the combustion of carbon that had been entrapped during the fritting stage of glaze formation. The glazes that come to a quiet fusion earliest are less likely to exhibit this defect. Raw feldspar glazes show this defect more than the raw Cornwall stone glazes, but as was shown by Mr. Coulter¹ the stone glazes are more fusible, and have a longer heat range, and therefore are subjected for a shorter time to the influence of carbon in the fire gases before quiet fusion sets in. As the evidence in this study in the case of fritted glazes agrees with similar phenomena observed in raw lead glazes, there seems to be no doubt that the statements in regard to the cause of pin-holing given above are correct.

In conclusion the writers wish to express their appreciation of the hearty support and substantial encouragement they received from the authorities of the University of Illinois in general, and from Professor C. W. Rolfe, Director of the Ceramic Department, in particular. Had they not granted every facility within their power, the ex-

¹Trans. Am. Cer. Soc. Vol. VII, p. 356.

cution of this study in its details would have been impossible. We wish also to express our further appreciation of the privilege of offering the results of this research to the American Ceramic Society previous to its issuance as a University Bulletin.

DISCUSSION.

The Chair: By the presentation of this very able paper, I am impressed at the outset with the growing importance of making provision, as soon as our financial condition shall warrant it, for the publication of such papers *prior to our meetings*, so that we may study them, and be better able to discuss them when we come to the meeting. We have realized this necessity during past sessions, but the need is growing more apparent all the time. Still this paper contains so many interesting points that we ought to have a general discussion on it.

Mr. Parmelee: I feel, of course, wholly unable to discuss the detail of this work. It certainly is a big subject, and I think brings pleasure to all members to see such a substantial contribution on it. Did I understand you to say, Mr. Fox, that coke was used as a fuel?

Mr. Fox: Yes, sir.

Mr. Parmelee: Then how do you attribute the pinholing to carbon deposited on the glaze? In what form is it deposited on the glaze?

Mr. Purdy: Coke certainly contains carbon, which on combustion is driven off. Not all the carbon, however, is oxydised to either carbon monoxide or carbon dioxide; some of it may be carried by the draft as particles of free carbon.

Mr. Parmelee: Then these are particles of fuel, carried mechanically and deposited mechanically?

Mr. Purdy: We know that black smoke contains about two percent. of carbon, and when the coke is freshly thrown on the grate bars there will be an evolution of smoke or black gases, and that is sufficient to cause a de-

posit of carbon on the glaze, notwithstanding the fact that the saggars are thoroughly sealed.

The Chair: You assume that in all of the kiln firings you formed this deposit, but in some were able to free the ware from it more completely than in others?

Mr. Purdy: No. When deposited prior to fusion, then the carbon would be incorporated and cause pinholing; but when deposited after the quiet stages of fusion has been reached, the glaze would not then be affected.

The Chair: But all appear to have the deposit in the earlier stage, but some are able to free themselves?

Mr. Purdy: No. Carbon is effective in producing pinholes only when it becomes incorporated into the glaze. If carbon is deposited on the glaze during the boiling period, it will become incorporated. A glaze which has its initial boiling period early, or which has a very short or mild boiling period, will not be affected as much as the glaze that boils later and consequently harder.

The Chair: I will ask Mr. Purdy what method he used to determine over-firing?

Mr. Purdy: We determined that by its appearance, i. e. when it began to pass into the second boiling stage. I do not know why it should boil the second time, but it does.

Mr. Parmelee: I have never had any experience in coke firing, but am surprised to learn that in burning coke you have black smoke.

Mr. Purdy: You will have some; and if you put one speck of carbon into the glaze at the period of troubled fusion, a pinhole will be the consequence, after the glaze is matured.

Mr. Plusch: Do these particles of carbon burn through and produce pinholes?

Mr. Purdy: Not in all cases.

Mr. Plusch: I find, in my experience, that carbon settling on the green ware before it is glazed, or settling on the glaze before the glaze is burned, does not produce pinholing in the firing. Very often particles fall on, after the pieces are sprayed, and we take no account of it.

Mr. Purdy: Carbon deposited either in or on the glaze before firing, will as a rule be burnt out before the glaze has reached its first boiling period. Hence you ought not to expect it to produce pin-holing under those conditions.

Mr. Gray: During the Boston meeting I brought up the question as to the appearance of pinholes in different parts of the kilns and at regular periods. I never found a probable solution until I made some experiments last fall, and I now believe the trouble is wholly in the carbon.

Mr. Plusch: In my experience I found that pin-holing occurred in the bottom of the kilns, especially when we fired quickly, or in other words, water-smoked too rapidly. I have entirely overcome this by water-smoking more slowly. Pin-holing on glazed terra cotta is also produced by the burning out of finely divided carbonaceous materials accidentally introduced into the body, or by the premature fusion of low-heat glaze materials introduced with the saggars used for grog.

In both of these cases cavities are produced on the surface of the ware, under the glaze, before it has matured, and show up on the burned ware as pinholes.

Mr. Purdy: In other words, you have overcome the pin-holing by permitting the carbon that is in the glaze to burn out, and by not permitting any more to deposit on the glaze after fusion has begun.

Mr. Hope: We fire with gas and there is no possible chance of having free carbon formed, yet we have pin-holing.

Mr. Purdy: You use a fritted glaze?

Mr. Hope: Yes. I put it down to the boiling of the glaze.

Mr. Goodwin: Did you say, Mr. Hope, that there were no fumes from the gas?

Mr. Hope: I meant that there was no uncombined carbon; that is, no free carbon in the kiln.

Mr. Goodwin: My experience goes to prove the contrary. I have seen smoke from gas, almost as from coal.

Mr. Hope: I accept the correction. I have seen the same thing myself, but failed to think of it in this connection, before.

Mr. Goodwin: I will ask Mr. Purdy if he has had experience in glazes high in Al_2O_3 , as to the probability of their spitting out?

Mr. Purdy: That is a matter with which I have had no experience.

Mr. Goodwin: I have found glazes of that nature inclined to spit out.

Mr. Millar: I make enameled bricks and burn in muffle kilns, and use a raw glaze and am not troubled much with pin-holing. But I find occasionally here and there throughout the kiln, bricks which are covered with pin-holes, while all around them, other bricks will be perfect. I have been trying to gather from Mr. Purdy's paper and remarks, what could be the cause of that, but I have not been able to do so.

Mr. Purdy: When I was working in the stoneware business, I found if the biscuit ware was not thoroughly brushed, we would have pinholes. The dust is sometimes common inorganic dirt and oftentimes it is soot or carbon. If that dirt was not brushed off, there would be pinholes as a consequence. But when the ware was thoroughly brushed, it would be free from pin-holing, provided we were careful not to smoke the kiln in the early stages of firing.

The Chair: In regard to this question of pin-holing, I had the question put to me some time since by a member, how to prevent it. Not working on Mr. Purdy's theory, but rather on one of my own which I presented to the society some two or three years ago, I said the way to prevent it was to be careful not to cool the kiln too rapidly. A sudden chill produces pin-holing, and we have been practically able to eliminate it from our ware, merely by a slow cooling. At the Cleveland summer meeting, while visiting a stoneware works in Akron where they were just firing off a kiln, the old burner was covering up every opening in sight. I asked him what he was doing? He said, "Why, if I don't

get this kiln closed tight as quickly as possible, the ware will be all pinholed." I attribute it, as I did in that paper, to the liberation of carbonic acid gas.

Mr. Purdy: In parts of this paper which were not read, we discuss how the probable reduction of lead in a glaze makes the glaze more viscous, and that the glaze does not fuse as readily as when free from the carbon, but that by continued soaking in the finishing heat, the normal condition would be re-produced, the carbon burned out, the lead oxydized, and we would have the glaze at its greatest fluidity, and consequently would not have pin-holing. In other words, carbon indirectly stiffens the glaze and prevents the healing over of these pinhole defects.

Besides this, pin-holing is probably not all due to one cause. There are probably other causes.

Mr. Binns: I am very glad we have drawn that confession from Mr. Purdy. I was afraid that he was committing himself to the opinion that this was the one and only cause, whereas everyone, I am sure, knows there are many causes. It is a new thought to me, that particles of carbon deposited on the surface of the glaze can cause pin-holing, and I was about to make other suggestions which Mr. Purdy's last remark renders unnecessary. I think it must be true that when carbon is deposited on the glaze in the early stages of the burn it is not deposited as particles but as a film, and I hardly see how a film of carbon should break into minute particles and cause pin-holing. The particles could not be carried in through the saggars, and the smoke deposited would be in the nature of a film. We must be cautious in claiming as facts what only appear as phenomena.

It is a pity we could not have seen the samples for this piece of work; apart from that, we have here a mass of material which it will take a long time to digest. I will ask what means were used to determine when a glaze was immature or when overfired? What is meant by an "over-fired" glaze? Is it a glaze which has proven too fluid, and has escaped control, or a glaze which has partly volatilized

and lost its beauty? This must be largely a matter of opinion. I do not know of any test by which a man can say a glaze is immature or overfired, and I think we ought to have Mr. Purdy's point of view on that point.

Mr. Purdy: In the case of our glazes, as the heat increased, the glaze passed gradually from a porous to a vitrified coating, then to that stage of bubbly fusion, then into quiet fusion. As soon as the glossiness of the glaze became dim by overheating, or as soon as the glaze began to show the second boiling, we called it overfired. We did not, however, have any dimness due to overfiring in our cases.

Mr. Goodwin: Do you mean that at the second boiling you got pin-holing?

Mr. Purdy: No; at that stage it looked like "curdled cream."

Mr. Goodwin: My experience has been that you can get pin-holing at the last stage as well as during the earlier stage, but it is of a different type.

Mr. Purdy: We explained that in a part of the paper which was not read, viz., that the pinholes due to overfiring seemed to go clear through and were larger, while the others, due to the carbon, were smaller, and apparently only surface phenomena.

as to produce a cloudy or milky appearance. When over-fired, the effect is similar to the curdiness produced in a glaze by addition of raw tin oxide. When fired to the best maturity of the glaze, the opalescent effects produced by supersaturation with SiO_2 are distinctly crystalline.

(5) While the writers have advanced the opinion that this opalescent effect is produced by supersaturation and separating out of SiO_2 , they can offer no evidence contradictory to the hypothesis that the material thus separated out is a borate. High content of B_2O_3 is required, and the opalescence here described not only does not appear unless B_2O_3 is proportionately high, but it increases in intensity and is produced in wider and wider variation as the B_2O_3 increases in proportion to SiO_2 . The writers have based their opinion that this phenomenon is due to the supersaturation of the glaze by SiO_2 , on the chemical composition of milky opals as they occur in nature.

ATTACK ON THE BODY.

The supposition has been advanced that Al_2O_3 is the principal constituent taken from the body by the glaze. The facts that support this assumption are as follows:

(1) The glazes lowest in Al_2O_3 (0.10—0.20 Eqv.) show this phenomenon to the greatest extent.

(2) The glazes lowest in Al_2O_3 show the fine-mesh crazing which results from incorporating constituents from the body into the glaze layer that is contiguous to the body, irrespective of oxygen ratio. It is a fact, however, that fine-mesh crazing decreases as the oxygen ratio increases, but this is attributed to the approximate saturation of the matrix with acid, as is evidenced in the appearance of opalescence as early as Group VI.

(3) Glazes having a low oxygen ratio, and low Al_2O_3 content, decrease in fine-mesh crazing as the intensity of heat increases.

(4) Glazes that craze in fine meshes when thick are crazed only in hair lines when thin.

(5) Increase of originally added Al_2O_3 decreases fine-mesh crazing under less intense temperatures, but increases it as the temperature becomes more intense.

(6) Fine-mesh crazing is certainly due to lack of homogeneity in the composition of the upper and lower surface of the glaze layer, and this lack of homogeneity is more pronounced, the more viscous the glaze is rendered by the incorporated constituent.

(7) Fine-mesh crazing developed at temperatures below Cone 5, can be counteracted by increasing the Al_2O_3 content of the glaze. If it is developed at higher heats, it can be counteracted by decreasing the Al_2O_3 content, especially when the oxygen ratio is low.

PIN-HOLING.

Pin-holing and blistering has been proven in these studies to be primarily due to the combustion of carbon that had been entrapped during the fritting stage of glaze formation. The glazes that come to a quiet fusion earliest are less likely to exhibit this defect. Raw feldspar glazes show this defect more than the raw Cornwall stone glazes, but as was shown by Mr. Coulter¹ the stone glazes are more fusible, and have a longer heat range, and therefore are subjected for a shorter time to the influence of carbon in the fire gases before quiet fusion sets in. As the evidence in this study in the case of fritted glazes agrees with similar phenomena observed in raw lead glazes, there seems to be no doubt that the statements in regard to the cause of pin-holing given above are correct.

In conclusion the writers wish to express their appreciation of the hearty support and substantial encouragement they received from the authorities of the University of Illinois in general, and from Professor C. W. Rolfe, Director of the Ceramic Department, in particular. Had they not granted every facility within their power, the ex-

¹Trans. Am. Cer. Soc. Vol. VII, p. 356.

cution of this study in its details would have been impossible. We wish also to express our further appreciation of the privilege of offering the results of this research to the American Ceramic Society previous to its issuance as a University Bulletin.

DISCUSSION.

The Chair: By the presentation of this very able paper, I am impressed at the outset with the growing importance of making provision, as soon as our financial condition shall warrant it, for the publication of such papers *prior to our meetings*, so that we may study them, and be better able to discuss them when we come to the meeting. We have realized this necessity during past sessions, but the need is growing more apparent all the time. Still this paper contains so many interesting points that we ought to have a general discussion on it.

Mr. Parmelee: I feel, of course, wholly unable to discuss the detail of this work. It certainly is a big subject, and I think brings pleasure to all members to see such a substantial contribution on it. Did I understand you to say, Mr. Fox, that coke was used as a fuel?

Mr. Fox: Yes, sir.

Mr. Parmelee: Then how do you attribute the pinholing to carbon deposited on the glaze? In what form is it deposited on the glaze?

Mr. Purdy: Coke certainly contains carbon, which on combustion is driven off. Not all the carbon, however, is oxydised to either carbon monoxide or carbon dioxide; some of it may be carried by the draft as particles of free carbon.

Mr. Parmelee: Then these are particles of fuel, carried mechanically and deposited mechanically?

Mr. Purdy: We know that black smoke contains about two percent. of carbon, and when the coke is freshly thrown on the grate bars there will be an evolution of smoke or black gases, and that is sufficient to cause a de-

posit of carbon on the glaze, notwithstanding the fact that the saggars are thoroughly sealed.

The Chair: You assume that in all of the kiln firings you formed this deposit, but in some were able to free the ware from it more completely than in others?

Mr. Purdy: No. When deposited prior to fusion, then the carbon would be incorporated and cause pinholing; but when deposited after the quiet stages of fusion has been reached, the glaze would not then be affected.

The Chair: But all appear to have the deposit in the earlier stage. but some are able to free themselves?

Mr. Purdy: No. Carbon is effective in producing pinholes only when it becomes incorporated into the glaze. If carbon is deposited on the glaze during the boiling period, it will become incorporated. A glaze which has its initial boiling period early, or which has a very short or mild boiling period, will not be affected as much as the glaze that boils later and consequently harder.

The Chair: I will ask Mr. Purdy what method he used to determine over-firing?

Mr. Purdy: We determined that by its appearance, i. e. when it began to pass into the second boiling stage. I do not know why it should boil the second time, but it does.

Mr. Parmelee: I have never had any experience in coke firing, but am surprised to learn that in burning coke you have black smoke.

Mr. Purdy: You will have some; and if you put one speck of carbon into the glaze at the period of troubled fusion, a pinhole will be the consequence, after the glaze is matured.

Mr. Plusch: Do these particles of carbon burn through and produce pinholes?

Mr. Purdy: Not in all cases.

Mr. Plusch: I find, in my experience, that carbon settling on the green ware before it is glazed, or settling on the glaze before the glaze is burned, does not produce pinholing in the firing. Very often particles fall on, after the pieces are sprayed, and we take no account of it.

Mr. Purdy: Carbon deposited either in or on the glaze before firing, will as a rule be burnt out before the glaze has reached its first boiling period. Hence you ought not to expect it to produce pin-holing under those conditions.

Mr. Gray: During the Boston meeting I brought up the question as to the appearance of pinholes in different parts of the kilns and at regular periods. I never found a probable solution until I made some experiments last fall, and I now believe the trouble is wholly in the carbon.

Mr. Plusch: In my experience I found that pin-holing occurred in the bottom of the kilns, especially when we fired quickly, or in other words, water-smoked too rapidly. I have entirely overcome this by water-smoking more slowly. Pin-holing on glazed terra cotta is also produced by the burning out of finely divided carbonaceous materials accidentally introduced into the body, or by the premature fusion of low-heat glaze materials introduced with the saggars used for grog.

In both of these cases cavities are produced on the surface of the ware, under the glaze, before it has matured, and show up on the burned ware as pinholes.

Mr. Purdy: In other words, you have overcome the pin-holing by permitting the carbon that is in the glaze to burn out, and by not permitting any more to deposit on the glaze after fusion has begun.

Mr. Hope: We fire with gas and there is no possible chance of having free carbon formed, yet we have pin-holing.

Mr. Purdy: You use a fritted glaze?

Mr. Hope: Yes. I put it down to the boiling of the glaze.

Mr. Goodwin: Did you say, Mr. Hope, that there were no fumes from the gas?

Mr. Hope: I meant that there was no uncombined carbon; that is, no free carbon in the kiln.

Mr. Goodwin: My experience goes to prove the contrary. I have seen smoke from gas, almost as from coal.

Mr. Hope: I accept the correction. I have seen the same thing myself, but failed to think of it in this connection, before.

Mr. Goodwin: I will ask Mr. Purdy if he has had experience in glazes high in Al_2O_3 , as to the probability of their spitting out?

Mr. Purdy: That is a matter with which I have had no experience.

Mr. Goodwin: I have found glazes of that nature inclined to spit out.

Mr. Millar: I make enameled bricks and burn in muffle kilns, and use a raw glaze and am not troubled much with pin-holing. But I find occasionally here and there throughout the kiln, bricks which are covered with pin-holes, while all around them, other bricks will be perfect. I have been trying to gather from Mr. Purdy's paper and remarks, what could be the cause of that, but I have not been able to do so.

Mr. Purdy: When I was working in the stoneware business, I found if the biscuit ware was not thoroughly brushed, we would have pinholes. The dust is sometimes common inorganic dirt and oftentimes it is soot or carbon. If that dirt was not brushed off, there would be pinholes as a consequence. But when the ware was thoroughly brushed, it would be free from pin-holing, provided we were careful not to smoke the kiln in the early stages of firing.

The Chair: In regard to this question of pin-holing, I had the question put to me some time since by a member, how to prevent it. Not working on Mr. Purdy's theory, but rather on one of my own which I presented to the society some two or three years ago, I said the way to prevent it was to be careful not to cool the kiln too rapidly. A sudden chill produces pin-holing, and we have been practically able to eliminate it from our ware, merely by a slow cooling. At the Cleveland summer meeting, while visiting a stoneware works in Akron where they were just firing off a kiln, the old burner was covering up every opening in sight. I asked him what he was doing? He said, "Why, if I don't

get this kiln closed tight as quickly as possible, the ware will be all pinholed." I attribute it, as I did in that paper, to the liberation of carbonic acid gas.

Mr. Purdy: In parts of this paper which were not read, we discuss how the probable reduction of lead in a glaze makes the glaze more viscous, and that the glaze does not fuse as readily as when free from the carbon, but that by continued soaking in the finishing heat, the normal condition would be re-produced, the carbon burned out, the lead oxydized, and we would have the glaze at its greatest fluidity, and consequently would not have pin-holing. In other words, carbon indirectly stiffens the glaze and prevents the healing over of these pinhole defects.

Besides this, pin-holing is probably not all due to one cause. There are probably other causes.

Mr. Binns: I am very glad we have drawn that confession from Mr. Purdy. I was afraid that he was committing himself to the opinion that this was the one and only cause, whereas everyone, I am sure, knows there are many causes. It is a new thought to me, that particles of carbon deposited on the surface of the glaze can cause pin-holing, and I was about to make other suggestions which Mr. Purdy's last remark renders unnecessary. I think it must be true that when carbon is deposited on the glaze in the early stages of the burn it is not deposited as particles but as a film, and I hardly see how a film of carbon should break into minute particles and cause pin-holing. The particles could not be carried in through the saggars, and the smoke deposited would be in the nature of a film. We must be cautious in claiming as facts what only appear as phenomena.

It is a pity we could not have seen the samples for this piece of work; apart from that, we have here a mass of material which it will take a long time to digest. I will ask what means were used to determine when a glaze was immature or when overfired? What is meant by an "over-fired" glaze? Is it a glaze which has proven too fluid, and has escaped control, or a glaze which has partly volatilized

and lost its beauty? This must be largely a matter of opinion. I do not know of any test by which a man can say a glaze is immature or overfired, and I think we ought to have Mr. Purdy's point of view on that point.

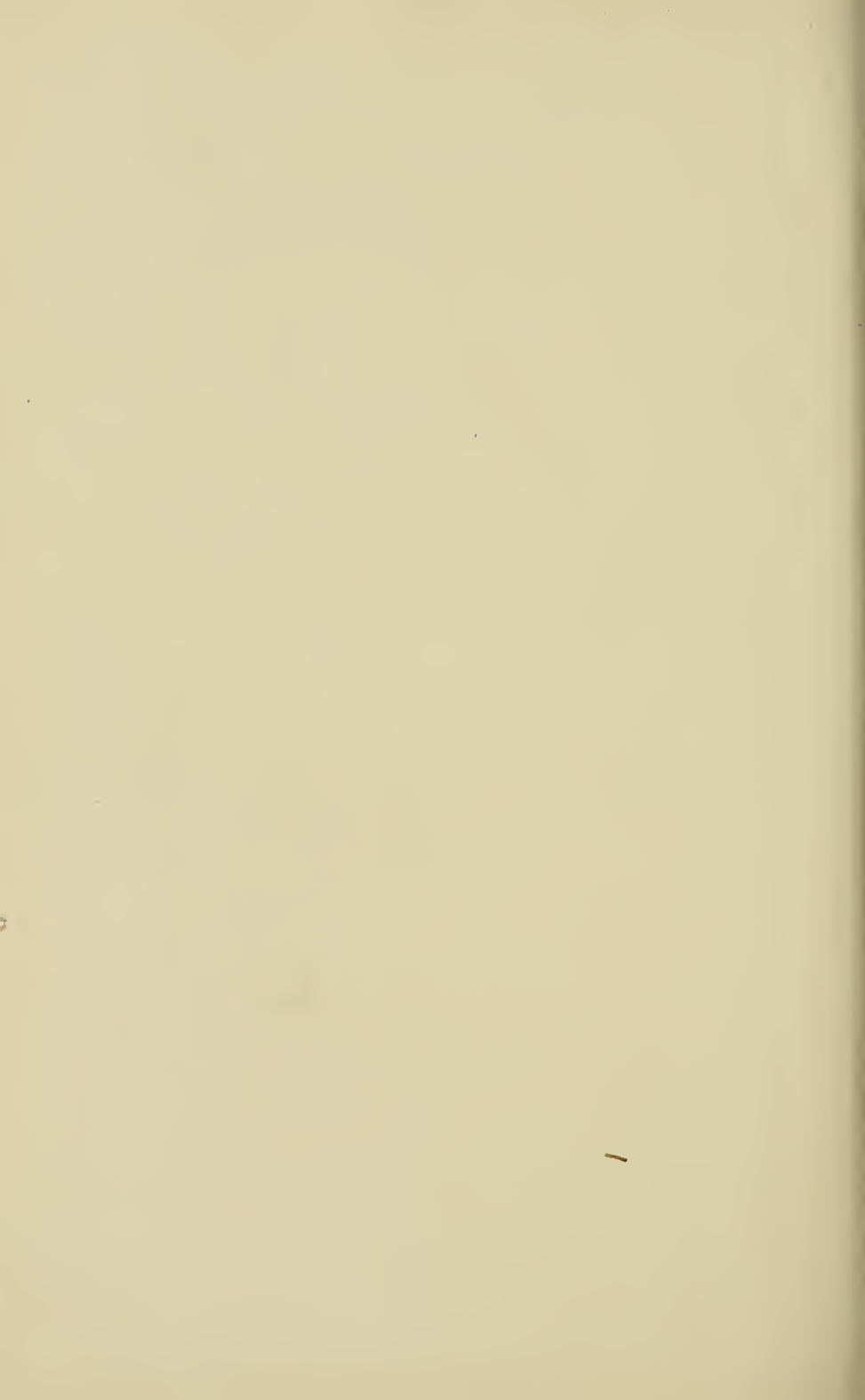
Mr. Purdy: In the case of our glazes, as the heat increased, the glaze passed gradually from a porous to a vitrified coating, then to that stage of bubbly fusion, then into quiet fusion. As soon as the glossiness of the glaze became dim by overheating, or as soon as the glaze began to show the second boiling, we called it overfired. We did not, however, have any dimness due to overfiring in our cases.

Mr. Goodwin: Do you mean that at the second boiling you got pin-holing?

Mr. Purdy: No; at that stage it looked like "curdled cream."

Mr. Goodwin: My experience has been that you can get pin-holing at the last stage as well as during the earlier stage, but it is of a different type.

Mr. Purdy: We explained that in a part of the paper which was not read, viz., that the pinholes due to overfiring seemed to go clear through and were larger, while the others, due to the carbon, were smaller, and apparently only surface phenomena.



UNIVERSITY OF ILLINOIS-URBANA



3 0112 052567101